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BY NATHAN S. OSBORNE AND MILTON S. VAN DUSEN.

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I. Introduction.

In reviewing the existing data on the thermodynamic properties of ammonia, the dearth of calorimetric measurements is at once apparent. Only when it is remembered that calorimetric data are of primary importance in the computation of tables adapted to the needs of the engineer can the difficulties of the computer be appreciated. With regard to the specific heat of liquid ammonia it appears that the experimental difficulty of measurement and the absence of urgent need for accurate values have deterred all but a few from the attempt. More recently the progress in the production of artificial refrigeration has led to a need for more accurate tables than those existing, and the measurement of the specific heat of liquid ammonia, together with other thermodynamic properties, has been undertaken in response to the expressed wish of the refrigeration industries.

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II. Previous Work.

The previous determinations of specific heat of liquid ammonia are represented graphically in Fig. 1, together with the results of the present measurements. None of the previous measurements extend to temperatures below 0°.

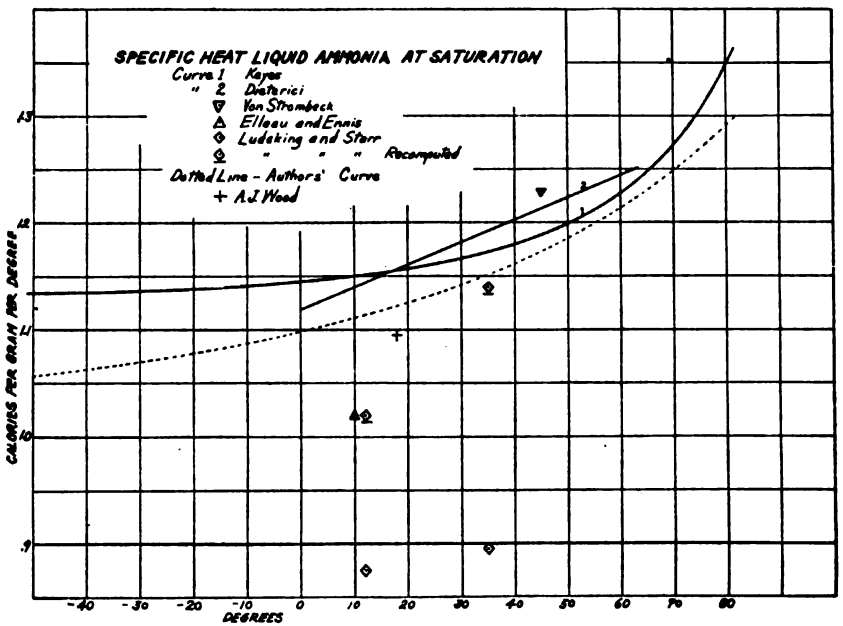

Fig. 1.

Von Strombeck[1] (1890) used the method of mixtures. About 128 g. of ammonia contained in a steel bomb were used in a calorimeter having a water equivalent of about 1 kg. The heat capacity from + 30° to + 60° was observed. Eight experiments were made.

Ludeking and Starr[2] (1893) employed a method similar to that of Von Strombeck but smaller apparatus. The total heat capacity of a steel shell of 16.12 cc. capacity containing 10.01 g. of ammonia was measured between +46° and +26°. It appears from present knowledge of the specific volume of liquid ammonia that at temperatures above 13° the liquid would have completely filled the container, and from the compressibility it may be estimated that at 46°, if the steel did not stretch considerably, the pressure within would have been in the neighborhood of 300 atmospheres. From the heat of compression of liquid ammonia it can be estimated that the heat capacity between 0° and 24° was approximately 15 % lower than it would have been under saturation condi-

[1] *J. Franklin Inst.*, 130, 467 (1890).

[2] *Phil. Mag.*, 35, 393 (1893); *Am. J. Sci.*, [3] 45, 200 (1893).

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tions and that between 26° and 46° it was about 21% lower. Both the published values and the values recomputed as indicated are shown in Fig. 1.

Elleau and Ennis[1] (1898) also used the method of mixtures between 0° and +25°. Nine grams of ammonia in a capsule of 20 cc. capacity were used.

Dieterici and Drewes[2] (1904) used the Bunsen ice calorimeter. The specimen of ammonia was inclosed in a sealed glass capsule of 1.2 cc. capacity.

A. J. Wood[3] (1912) used the method of mixtures with a sample of about 60 g. of ammonia. Six experiments were made between 16° and 20°.

Keyes and Brownlee[4] (1916) have given an equation based upon experimental work of Babcock.[5]

About 29 g. of ammonia were contained in a steel bomb of 52.65 cc. capacity. The heat capacity was determined with reference to water by a method of substitution in which a second identical bomb was adjusted to contain such an amount of water that the heat capacities of the two bombs were the same. The calorimetric method of mixtures was employed to measure the relative heat capacities. The calorimeter consisted of a Dewar vessel. An ingenious automatic device was used to transfer the bomb to the calorimeter from the preheater in a definite manner. The results of two determinations are given, being the mean specific heat capacities between 0° and 20°, and between 20° and 50°, respectively.

III. General Description of Apparatus and Method.

In carrying out the measurements of specific heat of the liquid two independent methods were used. In one method the heat added to a fixed amount confined in the calorimeter and the resulting change in temperature were measured under saturation conditions. By using independent data for the specific volumes of the two phases and for the latent heat of vaporization the correction for the heat used to change the temperature and amount of vapor present may be determined and the specific heat of the saturated liquid obtained.

In the other method the calorimeter is kept full of liquid at a constant pressure above saturation, the heat added to the variable quantity, and the resulting change in temperature measured, due consideration being paid to the amount and temperature of the expelled portion. The result of this method of measurement is to give the specific heat of the liquid at a constant pressure.

[1] *J. Franklin Inst.*, **145**, 189, 280 (1898).

[2] *Z. ges. Kalte Ind.*, **11**, 21, 47 (1904).

[3] *Ice Refrig.*, April, 1912.

[4] "Thermodynamic Properties of Ammonia," John Wiley & Sons, 1916.

[5] Keyes and Babcock, THIS JOURNAL, **39**, 1524 (1917).

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By using the independent data for the latent heat of pressure variation of the liquid, obtained from supplementary experiments with the same apparatus, the specific heat of the saturated liquid may be computed by general thermodynamic formulas, thus giving an independent check on the two methods of measurement.

The calorimeter used in making the experimental determinations having been previously described in detail elsewhere,[1] only a brief description is here given. The instrument is of the aneroid type and was specially designed to meet the requirements of this investigation. A metal shell of sufficient strength is made in the form of a cylinder having a re-entrant central tube. The interior annular space contains the material to be investigated. An electric heating coil and a resistance thermometer are located in the central tube. Heat developed in the coil is transmitted to the surrounding liquid, the distribution being favored by radial metal vanes. The interior of the shell is tinned and the outside nickeled. For preventing the transfer of unmeasured heat between this calorimeter and its environment it is suspended within a shield consisting of a thermally controlled jacket, with an air space between for thermal insulation. For evaluating the thermal leakage—that is, the heat exchanged with the surroundings by reason of temperature differences—multiple thermocouples with junctions distributed on the surfaces indicate temperature differences between calorimeter and jacket. Leakage is usually annulled by keeping the average jacket and calorimeter surface temperatures equal. The heat supplied to the calorimeter electrically is developed at a nearly constant rate in the heating coil by current from a storage battery. Temperature changes are measured either by the resistance thermometer in the calorimeter or by an auxiliary resistance thermometer in the envelope, using thermocouples for the transfer. The energy supplied is determined by potentiometer measurements of current and potential drop and by the duration of the heating current.

The material which is the subject of the measurement is introduced into the previously evacuated calorimeter through the tube provided for this purpose. The sample is confined in a special steel reservoir, which is closed by means of a valve. After being weighed the reservoir is suspended in an auxiliary thermoregulated bath and connected to the calorimeter. When the valves in this connection are open, the flow into the calorimeter is induced by vapor-pressure difference caused by heating the reservoir above the temperature of the calorimeter. If the connecting tube is made to extend down to the bottom of the reservoir the transfer occurs by liquid flow, while if this tube terminates at the top of the reservoir the transfer occurs by distillation. The removal of the material from the calorimeter, except in the case of actual overflow by expansion when al-

[1] Bur. of Standards, *Bull.* 14, 133 (1917); *Scientific Paper* No. 301.

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ready full of liquid, is necessarily by distillation, since the orifices are at the top. The large amount of heat transferred when distilling to or from the calorimeter can be readily extracted or added by use of the cooling device or the heating coil as needed.

IV. Material.

The material used in these determinations was prepared by McKelvy and Taylor of the chemical division of this Bureau by methods described in detail in an independent paper.[1] Abrief description of the process of preparation is here given.

A sample of commercial ammonia was transferred by distillation into a steel container which would hold about a kg. From this it was again transferred by distillation into a similar vessel containing metallic sodium, to remove any remaining traces of water. Following this dehydration, the purification was continued by from six to eight consecutive fractional distillations, the first and last tenths of each distillation being rejected. Removal of the rejected first fractions was performed in such a way as to extract the noncondensing gas present.

Two samples purified in the above manner, designated A and C, were used in the determination.

Sample A, used in the determinations by the first method, was made from commercial anhydrous ammonia manufactured from ammonium sulfate.

Tests showed the following impurities in this sample: Noncondensing gases in the vapor phase at 25°, 1 part in 10,000 by volume; water, 1 part in 10,000 by weight.

Sample C, used in the determinations by the second method, was made from commercial anhydrous ammonia manufactured by the synthetic method. The sample showed about the same proportion of noncondensing gases as Sample A.

V. First Method. Measurements under Saturation Conditions.

In the determinations by this method the ammonia contained in the calorimeter is part liquid and part vapor, and, therefore, the pressure is that of saturated vapor, and the state and relative amount of each phase when in equilibrium are completely defined by the temperature. The observations yield, as a direct result, the heat added to the contained ammonia per degree temperature rise. For the obvious purpose of minimizing the variation with temperature of the heat content of the vapor present, only enough vapor space is allowed when filling to insure a safe margin at all temperatures to be experienced.

The experimental data obtained from the observations made by the first method, together with the computations for obtaining the specific heat σ of the saturated liquid, are given in Table I. The computations

[1] To be published in the Bulletin of Bureau of Standards.

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TABLE I.

First Method.—Measurements of Specific Heat of Liquid Ammonia under Saturation Conditions.

Part 1.—Mass in Calorimeter, 274.33 G.

Experiment No.	$\Delta\theta$. Mean. Degrees.	Heat cap., calorimeter and contents. Joules/deg.	N. Heat capacity calorimeter. Joules/deg.	Heat cap. contents. $\frac{1}{M}\frac{\Delta Q}{\Delta\theta}$. J./g. deg.	$\frac{\theta_1+\theta_2}{2}=\theta_m$. Mean temperature. °C.	Correction term for vapor. J./g. deg.	Specific heat of liquid. c. J./g. deg.	Deviations from Equation A. J./g. deg.
1.....	10.007	2151.1	929.0	4.455	—38.68	—0.014	4.441	±0.000
2.....	9.8735	2175.2	941.8	4.496	—28.74	—0.016	4.480	+0.006
3.....	9.755	2197.4	953.8	4.534	—18.93	—0.019	4.515	+0.004
4.....	9.8225	2219.7	964.5	4.576	—9.13	—0.019	4.557	+0.004
5.....	9.7075	2242.4	974.8	4.620	+0.63	—0.019	4.601	+0.002
6.....	9.786	2221.0	965.0	4.578	—8.56	—0.019	4.559	+0.005
7.....	10.1605	2244.0	975.5	4.624	+1.42	—0.019	4.605	+0.002
8.....	10.047	2267.7	985.7	4.673	+11.52	—0.016	4.657	±0.000
9.....	10.428	2293.1	995.8	4.729	+21.76	—0.004	4.725	+0.002
10.....	10.306	2319.0	1005.8	4.787	+32.12	+0.015	4.802	+0.004
11.....	5.252	2129.7	918.5	4.415	—46.32	—0.010	4.405	—0.012
12.....	10.392	2150.4	929.3	4.451	—38.49	—0.014	4.437	—0.004
13.....	10.2685	2175.1	942.5	4.493	—28.16	—0.017	4.476	±0.000
14.....	10.151	2198.1	954.6	4.533	—17.95	—0.018	4.515	+0.001
15.....	10.040	2221.3	965.8	4.577	—7.86	—0.020	4.557	—0.001
16.....	10.099	2236.5	972.7	4.607	—1.33	—0.019	4.588	—0.002
17.....	9.989	2259.8	983.0	4.654	+8.72	—0.016	4.638	—0.004
18.....	9.876	2283.6	992.8	4.705	+18.65	—0.009	4.696	—0.007
19.....	9.760	2308.0	1002.3	4.760	+28.47	+0.008	4.768	—0.001
20.....	9.6465	2333.6	1011.3	4.820	+38.17	+0.028	4.848	±0.000
Part 2.—Mass Ammonia in Calorimeter, 274.72 G.								
21.....	9.4715	2153.1	929.0	4.456	—38.65	—0.014	4.442	+0.001
22.....	9.3655	2175.0	941.2	4.491	—29.23	—0.015	4.476	+0.003
23.....	9.267	2196.1	952.4	4.527	—19.92	—0.018	4.509	+0.002
24.....	9.168	2218.1	962.6	4.570	—10.70	—0.019	4.551	+0.005
25.....	9.7475	2220.3	964.2	4.572	—9.37	—0.019	4.553	+0.001
26.....	4.816	2236.3	972.0	4.602	—2.08	—0.019	4.583	—0.002
27.....	4.776	2247.9	976.8	4.627	+2.71	—0.019	4.608	—0.002
28.....	9.729	2258.0	981.7	4.646	+7.46	—0.016	4.630	—0.005
29.....	9.549	2147.1	926.2	4.444	—40.89	—0.013	4.431	—0.002
30.....	9.448	2169.2	938.5	4.480	—31.39	—0.015	4.465	±0.000
31.....	9.3425	2191.2	949.8	4.519	—21.96	—0.018	4.501	—0.002
32.....	9.237	2212.6	960.5	4.558	—12.70	—0.019	4.539	+0.002
33.....	9.140	2233.9	970.5	4.599	—3.51	—0.019	4.580	+0.001
34.....	9.105	2233.5	970.0	4.599	—4.00	—0.019	4.580	+0.003
35.....	8.983	2253.0	979.3	4.636	+5.05	—0.018	4.618	—0.004
36.....	8.8895	2274.1	988.3	4.680	+13.98	—0.014	4.666	—0.007
37.....	8.7915	2296.2	996.8	4.730	+22.82	—0.002	4.728	—0.001
38.....	8.707	2317.1	1005.4	4.775	+31.57	—0.015	4.790	—0.003
39.....	8.697	2315.8	1004.6	4.773	+30.85	+0.013	4.786	—0.001
40.....	8.5995	2337.7	1012.4	4.824	+39.49	+0.034	4.858	+0.002
41.....	4.250	2356.5	1018.2	4.872	+45.92	+0.054	4.926	+0.005

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are made by means of the following equation, derivation of which can be found in the original paper:[1]

$$\sigma = \frac{\Delta Q}{\Delta\theta}\frac{1}{M} - \frac{1}{\Delta\theta}\int_{\theta_1}^{\theta_2}\theta\frac{d}{d\theta}\left(\frac{Lx}{\theta}\right)d\theta.$$

ΔQ = heat added to ammonia.
$\Delta\theta$ = temperature change θ_1 to θ_2.
M = total mass in calorimeter.
L = latent heat of vaporization.
x = mass vapor in calorimeter per gram total.

The second term in this equation represents the correction for change in amount and temperature of the vapor.

The values of x, the dryness factor, or the mass of vapor per gram of ammonia in the calorimeter for each of the two fillings are shown graphically as functions of θ in Fig. 2.

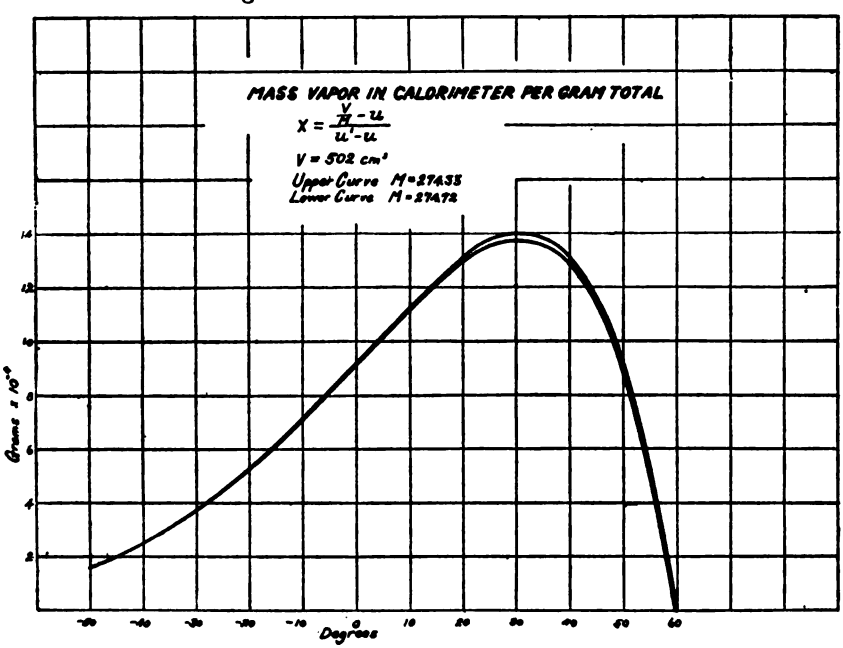

Fig. 2.

The value of the correction term for vapor used in the calculations of Table I was obtained graphically.

The volume V of the calorimeter was determined before the calorimeter was assembled by weighing empty and again filled with water at a known temperature. The variation in volume with temperature need not be known accurately. It was obtained from independent determinations of

[1] Bur. of Standards, *Bull.* 14, 397 (1917); *Scientific Paper* No. 313.

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the change in amount of liquid ammonia contained at various temperatures and pressures.

The values for the specific volumes of ammonia liquid and vapor are preliminary values from the measurements made at this Bureau by Harper, Cragoe, and O'Connor, the final results of which will be published in a separate paper.

The values of the latent heat of vaporization are from data published under a separate title.[1]

The results of the foregoing direct measurements of the specific heat of liquid ammonia under saturation conditions may be represented by the empirical equation

$$\sigma = 3.0931 - 0.00064\theta + \frac{17.329}{\sqrt{133 - \theta}} \qquad \text{(A)}$$

in which 133° is taken as the temperature at the critical point. The form of this equation is discussed in Section VII.

VI. Second Method. Measurements at Constant Pressure.

The primary object of this series of measurements was to afford a check upon the accuracy of the previous series of measurements under saturation conditions. In the first method distillation in the connecting tubes might occur, thus introducing an error[2] which could not be readily evaluated. The method of measurement at constant pressure, however, in which the tubes are kept filled with liquid, eliminates this possibility. The two methods are fundamentally independent. In the first method a fixed mass of material consisting of both liquid and vapor phases is confined in the calorimeter. The relative amounts of these two phases depend upon the temperature, and corrections involving a knowledge of the specific volumes and the latent heat of vaporization are therefore necessary. In the second method the liquid phase alone entirely fills the calorimeter space, and since the thermal expansion of the material differs from that of the calorimeter itself, the amount contained varies with the temperature. It was scarcely anticipated when the second method was undertaken that it would yield results comparable in precision with the first method, on account of greater experimental difficulty, although it was expected to disclose any serious error in the first method, due to distillation in the connecting tubes. As eventually carried out, however, this method gave a precision equal to that of the first, and the possible sources of systematic error, while different from those in the first method, appeared no greater.

[1] Osborne and Van Dusen, "Latent Heat of Vaporization of Ammonia," THIS JOURNAL, 40, 14 (1918).

[2] It is estimated that the maximum error due to this cause could not have exceeded 1 part in 1000, and that the average error was much less than this, but the comparison between the results of the two methods furnishes the most convincing evidence as to its limit.

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The computations for obtaining $[C_p]_{\text{Sat.}}$, the value of the constant pressure specific heat at the saturation limit, together with the specific heat σ of the saturated liquid, are given in Table II. The computations were made by means of the following equations, derivation of which can be found in the original paper:

$$[C_p]_{\text{Sat.}} = \frac{1}{M_m}\frac{\Delta Q}{\Delta\theta} - \frac{1}{M_m}\frac{\Delta M}{\Delta\theta}C_p\lambda - \theta\frac{d}{d\theta}\left(\frac{l}{\theta}\right)_p(p-\pi)$$

$$\sigma = [C_p]_{\text{Sat.}} + [l]_{\text{Sat.}}\, d\pi/d\theta$$

C_p = specific heat of liquid at constant pressure.
M_m = mass liquid in calorimeter at mean temperature.
λ = lag of outgoing liquid.
l = latent heat of pressure variation of liquid.
p = pressure in calorimeter.
π = saturation vapor pressure.

The pressure p corresponding to saturated vapor pressures at temeratures, θ_r, in the reservoir were obtained from data for pressure of saturated ammonia vapor given by Keyes and Brownlee.[1]

The values of the latent heat of pressure variation, l, used both in the calculation of $[C_p]_{\text{Sat.}}$ and of the specific heat of the saturated liquid σ were obtained from a series of measurements described elsewhere.[2]

TABLE II.

Second Method.—Measurements of Specific Heat of Liquid Ammonia at Constant Pressure.

Calculation of Specific Heat of Saturated Liquid Ammonia.

Experiment No.	Mean temperature. θ_m. °C.	Mass in calorimeter at mean temperature M_m. Grams.	Net heat added $\frac{1}{M_m}\frac{\Delta Q}{\Delta\theta}$. Joules/deg.	Corr. for heat to expelled liquid.	$\frac{d}{d\theta}\left(\frac{l}{\theta}\right)(p-\pi)$.	Specific heat at const. press. $[C_p]_{\text{Sat.}}$	Heat of pressure variation $[l]_{\text{Sat.}}\frac{d\pi}{d\theta}$	Specific heat at saturation. σ.	Derivations from Equation B.
				J./g. deg.	J./g. deg.	J./g. deg.	J./g. deg.	J./g. deg.	J./g. deg.
42	—38.95	345.64	4.440	+0.005	+0.002	4.447	—0.002	4.445	—0.002
43	—26.32	337.85	4.488	+0.005	0.003	4.496	0.005	4.491	+0.002
44	—15.90	331.36	4.530	+0.005	0.003	4.538	0.008	4.530	+0.001
45	—5.94	325.14	4.571	+0.005	0.007	4.583	0.012	4.571	±0.000
46	+5.00	317.78	4.628	+0.005	0.007	4.640	0.018	4.622	—0.001
47	+14.86	310.89	4.689	+0.005	0.008	4.702	0.026	4.676	—0.002
48	+18.05	308.43	4.717	+0.005	0.004	4.726	0.029	4.697	±0.000
49	+25.29	303.21	4.769	+0.005	0.006	4.780	0.038	4.742	—0.001
50	+35.72	295.28	4.868	+0.006	0.005	4.879	0.055	4.824	+0.003

[1] "Thermodynamic Properties of Ammonia," p. 13, John Wiley & Sons, 1916.

[2] "Latent Heat of Pressure Variation of Liquid Ammonia," Bur. of Standards, *Bull.* 14, 433 (1917); *Scientific Paper* No. 314.

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The values of the specific heat σ of the saturated liquid computed from the measurements made at constant pressure may be represented by the empirical equation

$$\sigma = 3.1800 - 0.00050\theta + \frac{16.356}{\sqrt{133-\theta}}. \qquad \text{(B)}$$

A comparison between the values of σ computed by this equation and those actually determined is given in the same table.

VII. Form of Empirical Equation for Specific Heat of the Saturated Liquid.

A form of empirical equation was sought which would closely fit the experimental data and which would also be consistent with other known physical facts. Keyes and Brownlee[1] have given an empirical equation for the specific heat of saturated liquid ammonia, the form of which they chose because "it seems probable that the heat capacity becomes infinite at the critical temperature." This conclusion appears as certain as any physical fact well can be which is not susceptible of direct experimental proof. It is, however, not of more importance than the manner of variation by which the infinite value is reached, and if used alone may easily lead to a form of empirical equation which gives the absurd result of an infinite value for the heat content of the liquid at the critical point. Therefore the limitation should also be imposed that the heat added for any finite temperature increment must be finite.

An empirical equation for σ over an extended range should, therefore, conform to two criteria in addition to adaptability to the experimental data, namely,

$$\sigma_c = \infty$$

$$\int_0^{\theta_c} \sigma d\theta \neq \infty$$

where θ_c is the temperature of the critical point.

An equation of the form $\sigma = A + B\theta + C/(\theta_c - \theta)^{1/2}$ has been found to meet these requirements, and has been used to represent the results of the present investigation. The equation has the further advantage of giving no real values above the critical temperature.

The form of equation used by Keyes and Brownlee[1] was found to be unsuited to represent these results; indeed, when applied to the data here given the constants found were such as to give a maximum for σ at about 100° and $-\infty$ at the critical temperature 133°.

VIII. Conclusions.

The results of the determinations by the two independent methods have been expressed by the following two empirical equations:

[1] "Thermodynamic Properties of Ammonia," John Wiley & Sons, 1916.

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First method: $$\sigma = 3.0931 - 0.00064\theta + \frac{17.329}{\sqrt{133 - \theta}} \qquad \text{(A)}$$

Second method: $$\sigma = 3.1800 - 0.00050\theta + \frac{16.356}{\sqrt{133 - \theta}} \qquad \text{(B)}$$

where the positive value of the square root is to be used.

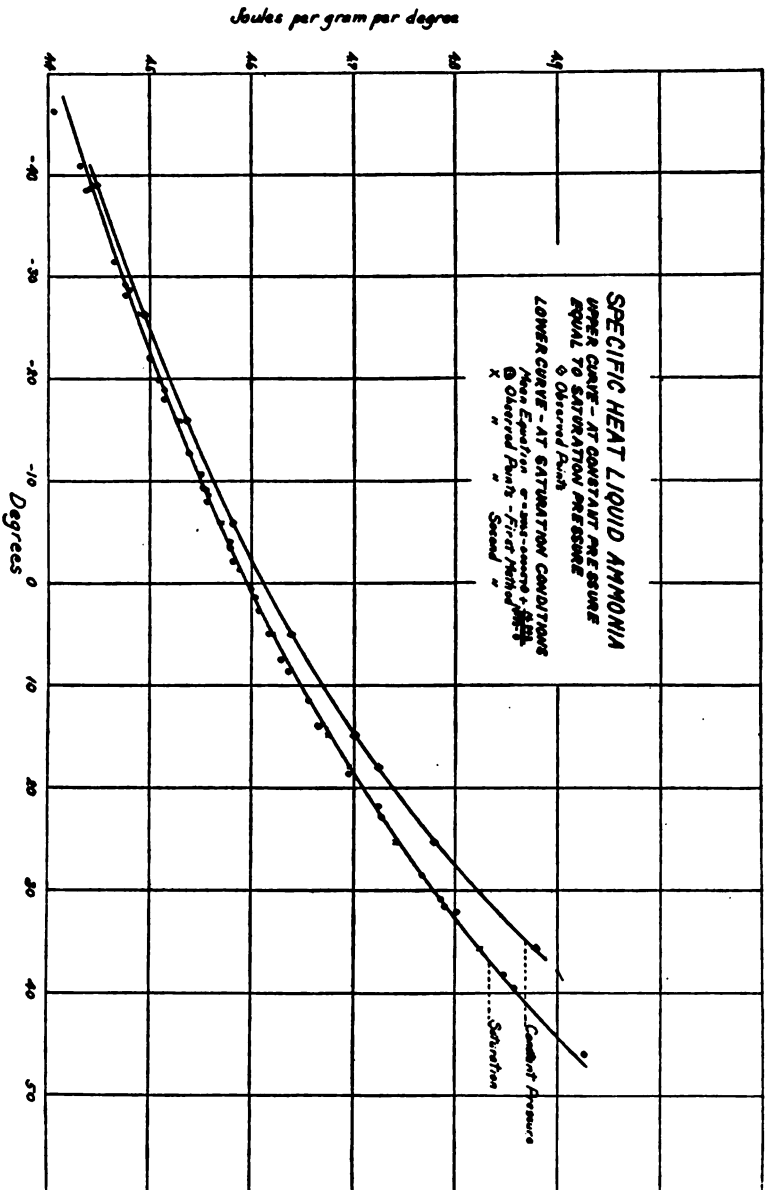

Fig. 3.

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The agreement of the results by two methods is shown by the following values computed from the equations:

Temperature.	—40°.	—20°.	0°.	20°.	40°.
Equation A.....	4.438	4.508	4.599	4.711	4.864
Equation B.....	4.444	4.513	4.599	4.710	4.856
Mean.....	4.441	4.510	4.599	4.710	4.860

The greatest difference between the mean results by both methods and the results of either method as represented by empirical equations is seen to be less than 1 part in 1000.

In Fig. 3 the results of all the determinations by both methods are shown graphically.

The order of accuracy of the two methods seems to be about the same, with a slight advantage in favor of the second. Giving each method equal weight, the final mean value of σ in joules per gram per degree is expressed in the range —45° to +45° by the equation

$$\sigma = 3.1365 - 0.00057\,\theta + \frac{16.842}{\sqrt{133 - \theta}}. \qquad \text{(C)}$$

If the relation between the joule and the 20° calorie[1] be taken as 1 calorie_{20} = 4.183 joules, the specific heat σ in Ca_{20}/g. deg., of liquid ammonia under saturation conditions is given by the equation

$$\sigma = 0.7498 - 0.000136\,\theta + \frac{4.0263}{\sqrt{133 - \theta}}. \qquad \text{(D)}$$

IX. Summary.

Using a calorimeter of the aneroid type specially designed for the peculiar conditions, the specific heat of saturated liquid ammonia has been determined throughout the temperature interval —45° to +45°.

A brief description of the instrument is given in this paper. A detailed description of the design and construction are given in a separate paper.

Two distinct and independent methods were used, each of which avoids sources of error present in the other. In the first method the heat added to a fixed amount confined in the calorimeter under saturation conditions and the resulting change in temperature are measured. By using data for the specific volumes of the two phases and the latent heat of vaporization, the corrections for the vapor are applied, giving the specific heat of the liquid kept saturated.

In the second method the calorimeter is kept full of liquid at a constant pressure. The heat added to the variable amount in the calorimeter and the resulting change in temperature are measured. A correction for the heat withdrawn in the expelled liquid is determined by special experiments.

[1] The 20° calorie is taken as the quantity of heat per gram (mass) per degree centigrade required to raise the temperature of water at 20° at normal atmospheric pressure.

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By use of the data for the latent heat of pressure variation of the liquid, obtained from separate measurements, made with the same apparatus and material, the corrections for pressure variation are applied, the result being to give a second determination of the specific heat of the saturated liquid.

The greatest difference between the mean results of both methods and the results of either method as represented by empirical equations is less than 1 part in 1000.

As a final result, the specific heat σ in joules per gram per degree centigrade, of liquid ammonia, kept saturated, at the temperature θ, is given in the range —45° to +45° by the equation

$$\sigma = 3.1365 - 0.00057\,\theta + \frac{16.842}{\sqrt{133 - \theta}}.$$

Appendix.

TABLE III.

Specific Heat of Liquid Ammonia under Saturation Conditions.

Expressed in Calories$_{20}$ per G. per Degree.

Temp. °.	0.	1	2.	3.	4.	5.	6.	7.	8.	9.
—40	1.062	1.061	1.060	1.059	0.058	1.058	1.057	1.056	1.055	1.055
—30	1.070	1.069	1.068	1.067	1.066	1.065	1.064	1.064	1.063	1.062
—20	1.078	1.077	1.076	1.075	1.074	1.074	1.073	1.072	1.071	1.070
—10	1.088	1.087	1.086	1.085	1.084	1.083	1.082	1.081	1.080	1.079
—0	1.099	1.098	1.097	1.096	1.094	1.093	1.092	1.091	1.090	1.089
+0	1.099	1.100	1.101	1.103	1.104	1.105	1.106	1.108	1.109	1.110
+10	1.112	1.113	1.114	1.116	1.117	1.118	1.120	1.122	1.123	1.125
+20	1.126	1.128	1.129	1.131	1.132	1.134	1.136	1.137	1.139	1.141
+30	1.142	1.144	1.146	1.148	1.150	1.152	1.154	1.156	1.158	1.160
+40	1.162	1.164	1.166	1.169	1.171	1.173	1.176	1.178	1.181	1.183

TABLE IV.

Heat Content of Saturated Liquid Ammonia.[1]

Calories per G.

Temp.°.	0.	1.	2.	3.	4.	5.	6.	7.	8.	9.
—40	—43.3	—44.3	—45.4	—46.4	—47.5	—48.6	—49.6	—50.7	—51.7	—52.8
—30	32.6	33.6	34.7	35.8	36.8	37.9	39.0	40.0	41.1	42.2
—20	21.8	22.9	24.0	25.1	26.2	27.2	28.3	29.3	30.4	31.5
—10	11.0	12.1	13.1	14.2	15.3	16.4	17.5	18.6	19.7	20.8
—0	0.0	1.0	2.2	3.3	4.4	5.5	6.6	7.7	8.8	9.9
+0	+0.0	+1.1	+2.2	+3.3	+4.4	+5.5	+6.7	+7.8	+8.9	+10.0
+10	11.1	12.2	13.4	14.5	15.6	16.7	17.9	19.0	20.1	21.3
+20	22.4	23.5	24.7	25.8	27.0	28.1	29.3	30.4	31.6	32.7
+30	33.9	35.0	36.2	37.4	38.5	39.7	40.8	42.0	43.2	44.4
+40	45.5	46.7	47.9	49.1	50.3	51.5	52.7	53.8	55.0	56.2

WASHINGTON, D. C.

[1] Heat content as used here is defined by the relation

$$H = \epsilon + pv$$

where H = heat content, taken as zero at the temperature of melting ice, ϵ = internal or "intrinsic" energy, and H, ϵ, and pv are all expressed in the same units.

[Reckoned from the temperature of melting ice.]

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[CONTRIBUTION FROM THE BUREAU OF STANDARDS.]

LATENT HEAT OF VAPORIZATION OF AMMONIA.

BY NATHAN S. OSBORNE AND MILTON S. VAN DUSEN.

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CONTENTS.—I. Introduction. II. Previous Determinations. III. General Description of Method. IV. Results of Measurements. V. Form of Empirical Equation. VI. Conclusions. VII. Summary. Appendix.—Specific Heat of Saturated Ammonia Vapor.

I. Introduction.

In tables of heat content of ammonia such as engineers require, the latent heat of vaporization constitutes the major part. Nevertheless, the direct measurements of this property are among the rarest of the available experimental data. This is attributable probably to the fact that the latent heat of vaporization may, by thermodynamic formulas, be computed from other properties, more easily measurable; however, the data which have heretofore been available for this calculation have not been of a precision such as to yield satisfactory values for the latent heat. The measurements here presented have been carried out in response to the requests of the associations of refrigerating engineers in this country for more accurate data upon which to base calculations for machinery using ammonia in the production of artificial refrigeration.

II. Previous Determinations.

Results of previous determinations of the latent heat of vaporization of ammonia are represented graphically in Fig. 1. The three curves also

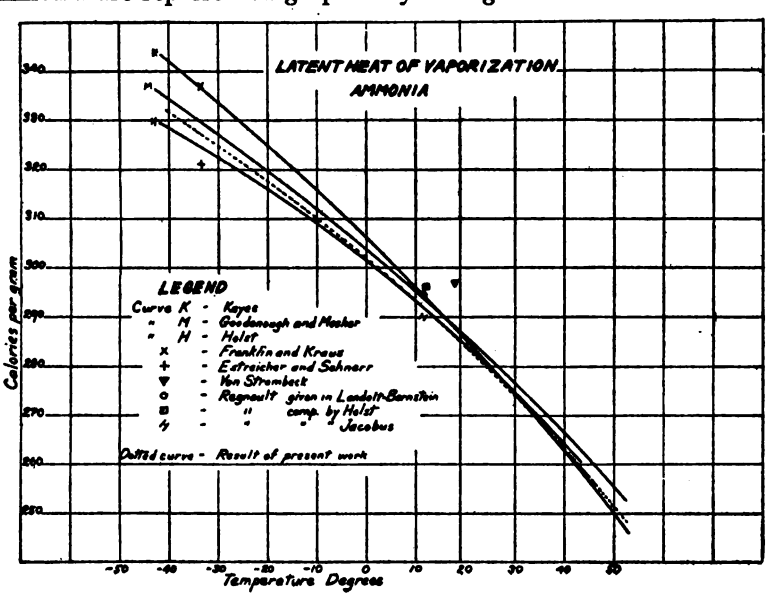

Fig. 1.

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shown in this figure represent values computed from other data by Keyes,[1] Goodenough and Mosher,[2] and Holst.[3]

Regnault[4] published a record of 12 experiments saved from the ruins of his laboratory, destroyed during the siege of Paris in 1870. The apparatus consisted of two calorimeters, the first, or evaporation calorimeter, in which the ammonia was allowed to evaporate from a steel container and flow through a chamber containing baffle plates, and the second, or expansion calorimeter, in which the ammonia vapor from the first calorimeter was allowed to expand to atmospheric pressure.

Regnault's results have been variously interpreted by different writers. Holst computed the latent heat of vaporization from the observation in the first calorimeter and ignored the partial expansion below saturation pressure which occurred there. As a mean result he obtained 296 calories per g. at 12°. Jacobus[5] computed the latent heat of vaporization from the observations in both calorimeters and obtained as a mean value 290 calories per g. at 12°. Landolt and Börnstein[6] give values from Regnault's data, the mean value at 12° being 294.5 calories per g.

Von Strombeck[7] used the same type of apparatus as Regnault and obtained from 12 experiments a mean value of 296.5 calories per g. at 18°.

Estreicher and Schnerr[8] (original paper unobtainable), according to Landolt and Börnstein, determined the heat of vaporization at the normal boiling point and obtained a value of 321 calories per gram at —33.4°.

Franklin and Kraus[9] determined the heat of vaporization at the normal boiling point. The apparatus consisted of a Dewar flask containing a liquid bath and a glass evaporating cell, each supplied with a platinum heating coil. The energy required to evaporate a certain volume of liquid ammonia was measured and the mass computed from the volume evaporated, using the value 0.604 for the density. The mean result from three experiments was 341 calories per g. Recomputed, using more recent date for the density (0.683), the mean value becomes 337 calories per g. This result is the same as that deduced by Franklin and Kraus from the absolute boiling point and the molecular elevation by vant Hoff's formula.

III. General Description of Method.

The calorimeter used in making the experimental determinations is the same as that described in a paper[10] on specific heat of liquid ammonia.

[1] "Thermodynamic Properties of Ammonia," John Wiley & Sons, 1916.

[2] Univ. of Ill., *Bull.* 66 (1913).

[3] Association Internationale du Froid, *Bull.* 51 (1915).

[4] *Ann. chim. phys.*, 24, 375 (1871).

[5] *Trans. Am. Inst. Mech. Eng.*, 12, 307 (1890).

[6] *Phys. Chem. Tabellen*, 1912.

[7] *J. Franklin Inst.*, 131, 470 (1891).

[8] *Bull. de l'Ac. de Cracovie*, p. 345 (1910); *Phys. Chem. Tables* (1912).

[9] *J. Phys. Chem.*, 11, 553 (1907).

[10] THIS JOURNAL, 40, 1 (1918).

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A system of baffle plates in the top of the calorimeter is provided for drying the vapor during its removal in evaporation experiments. The method employed in the determinations of heat of vaporization was to evaporate, slightly superheat, and withdraw from the calorimeter a measured amount of the ammonia. The approximate amount of heat required to effect this change was added and measured electrically, the small balance being due to the thermal leakage and the resulting change in temperature of the remainder of the system, both of which were kept relatively small and were measured. The jacket was kept at a constant temperature during the experiment. The withdrawn vapor passed into the reservoir, where it was condensed. The rate of outflow of the vapor was governed by the difference between the vapor pressures in the calorimeter and condenser and by the throttling at the needle valve in the connecting tube outside the calorimeter. This valve was provided with a graduated circle and index for facilitating fine adjustment. The vapor pressure in the condenser was controlled approximately by regulating its temperature. The balance between heat added and heat extracted from the system could be maintained in two independent ways—either by control of the outflow, using the regulating valve, or by control of the heat added electrically.

The temperature of the vapor withdrawn was determined with reference to the initial temperature of the experiment by means of the thermocouples attached to the outflow tube, the common reference junction being on the jacket. Three junctions equidistant along the length of the tube are available for this observation.

The pressure within the calorimeter was indicated by means of a closed manometer, the connection to the interior being similar to that used for transfer of ammonia. This manometer might have been calibrated in terms of actual pressures; but it was found, instead, more convenient to calibrate and use it as a vapor-pressure thermometer to indicate the temperature at the free surface of the liquid in the calorimeter, especially as the evaporation temperature—that is, the free surface temperature during evaporation—enters as a correction factor into the calculation of the final result.

Initially, the system consisting of the calorimeter and the ammonia sample is in thermal equilibrium, the contents comprising both liquid and vapor phases. A portion is withdrawn as superheated vapor with the addition of heat electrically and the remaining portion allowed to resume equilibrium; the aim being to adjust the rate of adding heat and the rate of evaporation so as to avoid large temperature changes throughout the process and to make the final temperature approximately equal to the initial. The initial and final temperatures and amount removed are ob-

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served, and periodic observations made throughout the experiment of the following quantities:

1. Current in electric heating coil.
2. Potential drop in heating coil.
3. Temperature difference between calorimeter and jacket surfaces.
4. Vapor pressure in calorimeter.
5. Temperature of vapor as it leaves the calorimeter at the pressure existing therein.

Given these data and the necessary additional data from independent sources, the problem is to compute the latent heat of vaporization.

The process which goes on in the calorimeter cannot be followed in detail, for during the period while heat is being added and vapor is being withdrawn the temperature is certainly not uniform and, furthermore, the temperature distribution in the ammonia is unknown. The observations during this period furnish merely knowledge at any instant of the temperature θ_e of the liquid surface at which the evaporation is occurring, and the temperature θ_s to which the vapor is superheated when withdrawn. It is thus evidently impossible to analyze in detail the phenomena which actually occur and recourse must therefore be had to some other method of interpreting the observations quantitatively. By assuming an ideal process which would, if carried out, lead from the observed initial to the observed final state and involve the same amount of external work as the actual process, the amount of heat required can be expressed in terms of known data and of the unknown latent heat of vaporization which is to be determined. If this expression be equated to the observed quantity of heat supplied during the actual experiment, the result after making certain minor approximations, is an equation from which the unknown latent heat L may be found. The notation used and the equation are as follows:

V = volumetric capacity of calorimeter in cubic centimeters.

M_1, M_2 = initial and final mass in calorimeter.

ΔM = mass, in grams, removed from calorimeter as superheated vapor. $\Delta M = M_1 - M_2$.

θ_1, θ_2 = initial and final temperatures of calorimeter and contents when in equilibrium.

$\bar{\theta}_e$ = average temperature of free surface in calorimeter.

$\bar{\theta}_s$ = average temperature of superheated vapor as it leaves the calorimeter.

ΔQ = heat added to contents of calorimeter during an experiment.

C_p' = specific heat at constant pressure p and temperature θ.

σ = specific heat, in joules per gram per degree, of the saturated liquid—that is, the liquid in equilibrium with the vapor.

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σ' = specific heat, in joules per gram per degree, of the saturated vapor.

u = specific volume in cm.^{3}/g. of the saturated liquid.

u' = specific volume in cm.^{3}/g. of the saturated vapor.

π = saturation pressure.

L = latent heat of vaporization at temperature θ in joules per gram, defined as the heat required to change 1 gram of saturated liquid to saturated vapor at a constant temperature and pressure.

$$L_1 = \frac{\Delta Q}{\Delta M} - L_1 \frac{u_1}{u'_1 - u_1} - \left(\sigma + \frac{dL}{d\theta} + \frac{L}{\theta}\frac{u}{u'-u}\right)(\bar{\theta}_e - \theta_1) - C'_p(\bar{\theta}_s - \bar{\theta}_e)$$
$$- \left\{\frac{M_2}{\Delta M}\left[\sigma - \theta\frac{d}{d\theta}\left(\frac{L}{\theta}\frac{u}{u'-u}\right)\right] + \frac{V}{\Delta M}\theta\frac{d}{d\theta}\left(\frac{L}{\theta}\frac{1}{u'-u}\right)\right\}(\theta_2 - \theta_1). \quad (1)$$

The expression, $\frac{\Delta Q}{\Delta M} - L_1 \frac{u_1}{u'_1 - u_1}$, in Equation 1 represents the quantity of heat which would be added to the ammonia per gram evaporated at the initial temperature θ_1. It would equal the latent heat of vaporization at that temperature if the experiment proceeded under ideal conditions, such that the heat added was instantaneously distributed over the free surface so as to avoid any change in temperature and pressure whatever, for then all the other terms would vanish. The remaining terms in the right member of Equation 1 represent corrections to the above expression for the departure of the actual experiment from the ideal conditions just specified.

Considerable variation in the manipulation was possible and such variations were purposely introduced as a means of detecting possible systematic errors. Experiments were made in which the aim was to keep the temperature of evaporation as nearly as possible equal to the initial temperature. In these experiments the thermal leakage was relatively large. Usually the thermal leakage was kept small by keeping the average surface temperature of the calorimeter nearly constant, and permitting the temperature of evaporation to vary. Different rates of evaporation were used as a test for the dryness of the vapor, on the supposition that if spray were carried out with the vapor the amount would vary with the rate. Different parts of the heating coil were used, that part usually being used which would develop the heat nearest to the place where evaporation occurred.

Some significant discrepancies in the earlier results were found to be due to the condensation of ammonia in the outflow tubes previous to beginning an experiment. Such an occurrence would result in transferring to the condenser more material than was evaporated during the period in which the heat added was measured and would therefore lead to a too low

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result for the latent heat of vaporization. This source of error was detected through the peculiarity that the initial experiment of a series frequently gave a result lower than those immediately following, the discrepancy in some cases being as much as 0.3 per cent. An error of this magnitude might be tolerated, but after identifying the cause an effective remedy was evident, namely, to precede the first determination in a day's series with a blank experiment by which all liquid condensed in the outflow tube during the preliminary cooling would be expelled and the tube dried. The results of all previous initial experiments where this procedure had been omitted should, of course, be excluded from the authentic determinations because, even when operating at low temperatures, although the natural tendency would be for the tube ultimately to become dry, nevertheless there was no assurance that sufficient time had elapsed for this to occur, and therefore all unpreceded experiments in a series are open to doubt.

The sample of ammonia used in these determinations was similar to Sample C, described in preceding paper.

IV. Results of Measurements.

The data obtained from the calorimetric measurements are given in Table I. ΔQ, the heat added to the ammonia, is computed according to the formula

$$\Delta Q = \Sigma(IEt') + Bht_2 - N(\theta_2 - \theta_1).$$

The total energy supplied electrically, $\Sigma(IEt')$, is the sum of the amounts for all the periods of heating during the experiment. In most of the experiments the energy was supplied during a single period, t', the current I and potential drop E being very nearly constant, so that the product of the average values obtained from the periodic readings of the potentiometer multiplied by the time t' gives the total energy within the limit of significant error. For the few experiments where the energy was supplied in several installments, each portion was computed separately and the sum taken. The thermal leakage was computed on the basis of the coefficient of thermal leakage B, determined by supplementary experiments, the average deflection of the galvanometer h and the total time t_2 elapsing between the initial and final readings of temperature θ_1 and θ_2. The energy absorbed by the calorimeter was computed on the basis of the heat capacity of the calorimeter N, determined by supplementary experiments, and the total change in temperature $\theta_2 - \theta_1$ during the experiment.

In Table II is given the computation of the latent heat of vaporization L from the experimental data in Table I, and accessory data from other sources. The computation in Table II is made according to Equation 1. This equation involves in addition to the data of the present experiments only the specific volumes u and u' of the two phases and the specific heat C_p' of the vapor at constant pressure.

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TABLE I.—CALORIMETRIC DATA.

Experiment No.	Heat to ammonia ΔQ. Joules.	Mass ammonia removed ΔM. G.	Final mass in calorimeter M_2. G.	$\frac{M_2}{\Delta M}$.	$\frac{V}{\Delta M}$. Cm.³/G.	Initial temperature θ_1. °C.	$\theta_2-\theta_1$. °C.	$\theta_4-\theta_1$. °C.	$\theta_5-\theta_4$. °C.
1	25 272	19.619	176.72	9.008	26	—5.39	—0.004	—0.10	+0.66
2	25 354	19.610	157.11	8.012	26	—5.40	+0.127	—1.23	+1.11
3	25 578	19.950	137.16	6.875	25	—5.27	—0.142	—1.10	+1.01
4	17 864	13.940	108.48	7.782	36	—4.84	—0.143	—2.23	+1.61
5	24 800	19.285	54.76	2.839	26	—4.98	+0.018	—1.17	+0.99
6	24 777	19.228	35.53	1.848	26	—4.96	+0.150	—0.69	+0.75
7	24 150	18.188	211.03	11.603	28	—21.83	—0.169	—1.95	+1.55
8	14 239	10.625	157.14	14.790	47	—22.09	+0.033	—0.29	+0.53
9	13 432	10.079	137.62	13.654	50	—22.48	—0.096	—0.50	+0.68
10	27 821	20.775	116.84	5.624	24	—22.58	—0.004	—1.32	+1.30
11	26 606	19.297	78.38	4.062	26	—35.75	+0.034	—0.95	+1.05
12	20 370	17.035	28.65	1.682	30	+22.23	+0.047	—0.81	+0.85
13	22 664	18.976	210.97	11.122	27	+20.84	—0.081	—0.77	+0.60
14	23 605	19.667	170.90	8.690	26	+20.38	—0.026	—0.85	+0.98
15	23 432	19.521	151.38	7.755	26	+20.35	—0.041	—0.33	+0.79
16	22 676	18.870	126.51	6.704	27	+19.74	—0.020	—0.44	+0.53
17	25 003	20.110	103.89	5.166	26	+7.60	—0.068	—0.54	+0.59
18	24 436	19.612	84.28	4.297	26	+7.53	+0.021	—0.63	+0.69
19	16 220	13.014	50.51	3.881	39	+7.38	—0.001	—0.25	+0.52
20	22 303	17.367	15.85	0.913	29	—4.09	+0.059	—0.35	+0.64
21	11 150	8.684	7.16	0.824	58	—4.03	+0.021	—0.48	+0.73
22	13 004	9.323	226.66	24.312	54	—42.01	—0.007	—0.63	+0.79
23	13 067	9.494	217.17	22.874	53	—42.01	—0.184	—0.43	+0.65
24	14 954	11.036	195.05	17.674	46	—28.28	—0.031	—0.39	+0.60
25	14 913	11.002	184.05	16.730	46	—28.31	—0.005	—0.44	+0.68
26	12 310	9.396	165.51	17.615	53	—14.93	—0.091	—0.44	+0.78
27	12 313	9.394	156.11	16.618	54	—14.70	—0.071	—0.60	+0.80
									$\theta_5-\theta_4$
28	11 921	10.485	134.94	12.870	48	+36.43	—0.061	....	+0.36
29	11 589	10.807	113.17	10.472	46	+51.80	—0.054	....	—0.02
30	11 989	11.112	90.92	8.182	45	+50.61	—0.042	....	—0.01
31	11 926	11.049	79.87	7.229	46	+50.56	+0.037	....	+0.03
32	11 831	10.934	68.94	6.305	46	+50.53	+0.006	....	+0.07
33	11 618	10.185	46.49	4.565	49	+36.21	+0.018	....	+0.19
34	11 652	10.214	36.28	3.551	49	+36.22	—0.012	....	+0.24

The following abbreviations are employed in the computations:

$$\frac{dH'}{d\theta} = \frac{dL}{d\theta} + \sigma + \frac{L}{\theta}\frac{u}{u'-u}$$

$$Y = \theta\frac{d}{d\theta}\left[\frac{L}{\theta}\frac{1}{u'-u}\right]$$

$$Z = \sigma - \theta\frac{d}{d\theta}\left[\frac{L}{\theta}\frac{u}{u'-u}\right]$$

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The values used for the specific volumes of the liquid and vapor phases of ammonia are preliminary values from the measurements made at this Bureau by Messrs. Harper, Cragoe, and O'Connor, the final results of which will be published in a separate paper.

TABLE II.—CALCULATION OF L_1.

Experiment No.	$\frac{\Delta Q}{\Delta M}$. Joules/g.	$L_1 \frac{u_1}{u'_1 - u_1}$. Joules/g.	$\frac{dH'}{d\theta}(\bar{\theta}_e - \bar{\theta}_1)$. Joules/g.	$C_{p'}(\bar{\theta}_e - \bar{\theta}_2)$. Joules/g.	$\frac{M_2}{\Delta M} Z(\theta_1 - \theta_2)$. Joules/g.	$\frac{V}{\Delta M} Y(\theta_1 - \theta_2)$. Joules/g.	L_1. Joules/g.	θ_1. °C	Deviation from Equation. Parts in 10,000.
1	1288.1	5.7	—0.1	1.5	—0.2	—0.0	1281.2	—5.33	+3
2	1293.0	5.7	1.5	2.6	+4.4	+0.4	1281.4	—5.40	+2
3	1282.1	5.7	1.3	2.4	—4.3	—0.4	1280.0	—5.27	—5
4	1281.5	5.8	2.7	3.8	—4.9	—0.6	1280.1	—4.84	+8
5	1286.0	5.8	1.4	2.3	+0.2	+0.0	1279.1	—4.98	—4
6	1288.6	5.8	0.8	1.7	+1.2	+0.5	1280.2	—4.96	+5
7	1327.8	3.0	2.8	3.4	—8.6	—0.3	1333.1	—21.83	—8
8	1340.1	3.0	0.4	1.1	+2.1	+0.1	1333.2	—22.09	—7
9	1332.7	2.9	0.8	1.5	—5.7	—0.4	1335.2	—22.48	—7
10	1339.2	2.9	1.9	2.8	—0.1	—0.0	1335.5	—22.58	—7
11	1378.8	1.6	1.5	2.2	+0.7	+0.0	1375.8	—35.75	+3
12	1195.8	14.2	0.5	2.2	+0.3	+0.3	1179.3	+22.23	+8
13	1194.6	13.7	0.5	1.6	—3.9	—0.4	1184.1	+20.84	+1
14	1200.2	13.5	0.6	2.5	—1.0	—0.4	1186.2	+20.38	+3
15	1200.3	13.5	0.2	2.1	—1.4	—0.2	1186.5	+20.35	+7
16	1201.7	13.2	0.3	1.4	—0.7	—0.1	1188.2	+19.74	—2
17	1243.3	8.9	0.5	1.5	—1.5	—0.3	1235.2	+7.60	+1
18	1246.0	8.9	0.6	1.7	+0.4	+0.1	1235.5	+7.53	+1
19	1246.3	8.9	0.2	1.3	—0.0	—0.0	1236.3	+7.38	+3
20	1284.2	6.0	0.4	1.5	+0.2	+0.2	1276.7	—4.09	+1
21	1284.0	6.0	0.6	1.7	+0.1	+0.1	1276.7	—4.03	+2
22	1394.8	1.2	1.0	1.6	—0.7	—0.0	1393.7	—42.01	+6
23	1376.3	1.2	0.7	1.3	—18.4	—0.3	1393.2	—42.01	+3
24	1355.0	2.3	0.6	1.3	—2.4	—0.1	1354.5	—28.28	+7
25	1355.5	2.3	0.7	1.4	—0.4	—0.0	1352.9	—28.31	—6
26	1310.1	4.0	0.6	1.7	—7.1	—0.4	1312.5	—14.93	±0
27	1310.8	4.0	0.8	1.8	—5.2	—0.3	1311.3	—14.70	—4
28	1137.0	21.3	0.1	2.5	—3.4	—0.8	1117.5	+36.43	+3
29	1072.4	32.2	+0.1	1.5	—2.4	—0.9	1041.9	+51.80	—6
30	1078.9	31.0	0.0	1.5	—1.5	—0.6	1048.5	+50.61	—1
31	1079.4	31.0	0.0	1.5	—1.1	—0.6	1048.6	+50.56	—3
32	1082.0	31.0	0.0	1.8	+0.1	+0.1	1049.0	+50.53	—1
33	1140.8	21.1	—0.1	2.0	+0.3	+0.2	1117.3	+36.21	—7
34	1140.8	21.1	0.1	2.0	—0.2	—0.2	1118.2	+36.22	+1

For the experiments where $\theta_e - \theta_1$ was not observed on account of the temperature being higher than would allow the use of the manometer, the value of $\theta_e - \theta_1$ was taken equal to 0.5°, this being the mean value in

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previous experiments. The greatest deviation from this value in the preceding experiments was not more than 0.3°, and this amount would not change the computed value of L more than 1 part in 1000. The final results probably are affected less than one-third this amount.

V. Form of Empirical Equation.

An empirical equation the form of which is consistent with the behavior of substances at the critical point should give a value of zero at the critical point for L, and for the derivative $dL/d\theta$ should give a value of $-\infty$. An equation of the form

$$L = A(\theta_c - \theta) + B(\theta_c - \theta)^{1/2},$$

in which θ_c = the critical temperature, was found to meet these requirements and to represent the experimental results closely. The equation has the further advantage of giving no real roots above the critical temperature.

VI. Conclusions.

An inspection was made to ascertain whether the results were affected by such variations as occurred in the experiments. The following conditions which might conceivably independently affect the results are: (*a*) Rate of evaporation; (*b*) thermal leakage; (*c*) average deviation of evaporation temperature from initial temperature; (*d*) maximum deviation of evaporation temperature from initial temperature; (*e*) portion of heating coil used; (f) amount removed; (*g*) amount in calorimeter (mean during experiment); and (*h*) temperature of experiment.

These various conditions were not all systematically changed one at a time, keeping all the others constant, as would have been necessary if large variations had been found to result from the changes. Except for the actual temperature of the determination, which is the primary independent variable, effects of variations in the other conditions are presumed to have been either eliminated experimentally or taken into account quantitatively in the computation of the results, supposing, of course, that such variations were kept within reasonable limits. If the results were dependent to a significant extent on these incidental conditions, it would scarcely be possible to avoid some effect being observed. By examination of the deviations from the value given by the empirical equation it has not been possible to trace any systematic deviation to any of the experimental conditions other than the temperature of the experiment. It may, therefore, be concluded that no systematic error resulted from these conditions which was not obscured by accidental errors.

Particular mention might be made of the rate of evaporation. If this rate were increased to the point where active boiling occurred, it is possible that the system of baffle plates might have failed to intercept all of the fine spray thrown up and the evaporation of the withdrawn material

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would have been incomplete, or, in other words, the vapor would have been wet. It is, therefore, of especial interest to note that considerable variation in rate occurred without causing any consequent effect upon the resulting value for latent heat, indicating that within the range of variation used the vapor was dry. Additional confirmation on this point is furnished by the fact that the temperature of the vapor withdrawn was, with rare exceptions, always higher than the temperature at which evaporation was proceeding within the calorimeter.

The results of the determinations may be expressed by means of the following empirical equation:

$$L = 137.91 \sqrt{133 - \theta} - 2.466 (133 - \theta)$$

VII. Summary.

Using a calorimeter of the aneroid type specially designed for the peculiar conditions, the latent heat of vaporization of ammonia has been determined throughout the temperature interval —42 to + 52°.

The instrument contains no special liquid for a calorimetric medium, the ammonia being the only liquid in the calorimeter. Heat developed and measured electrically in a coil is transmitted by conduction and convection to the surrounding ammonia and is utilized to effect the evaporation of a determined amount of the ammonia which is withdrawn as superheated vapor at a determined temperature and pressure. Heat from other sources is minimized by reducing as far as practicable the avenues for heat transfer between the calorimeter and its environment, and by so manipulating as to keep the temperatures of the calorimeter and jacket surfaces nearly equal, means being provided for determining the amount of thermal leakage which is not thus annulled. Initial and final temperatures are measured by a platinum resistance thermometer.

An analysis of the process occurring in the calorimeter during an experiment leads to a method of calculation of the results whereby data from other sources than the direct calorimetric observations enter only in the computation of correction terms which can by careful manipulation be made small.

Variations in manipulation were introduced as a means of detecting possible systematic errors, particularly in regard to the matter of dryness of the vapor withdrawn.

The result of each of the 34 determinations agrees with the mean result as expressed by means of an empirical equation within 1 part in 1000. An empirical equation was found which, in addition to representing closely the results in the range of temperature covered experimentally, also conforms to what is known about the behavior of substances in general when approaching the critical point.

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As a final result the latent heat of vaporization of ammonia—that is, the heat in joules per g. required to convert saturated liquid into saturated vapor at constant temperature—is expressed in the range —42° to +52° by the equation

$$L = 137.91\sqrt{133 - \theta} - 2.466\,(133 - \theta).$$

If the latent heat of vaporization be expressed in calories$_{20}$ per g. taking 1 calorie$_{20}$ = 4.163 joules, the equation becomes

$$L = 32.968\sqrt{133 - \theta} - 0.5895\,(133 - \theta).$$

The values computed from this equation in every degree are as follows:

CALORIES PER GRAM.

Temperature.	0.	1.	2.	3.	4.	5.	6.	7.	8.	9.
—40°	331.7	332.3	333.0	333.6	334.3	334.9	335.5	336.2	336.8	337.5
—30	324.8	325.5	326.2	326.9	327.6	328.3	329.0	329.7	330.3	331.0
—20	317.6	318.3	319.1	319.8	320.6	321.3	322.0	322.7	323.4	324.1
—10	309.9	310.7	311.5	312.2	313.0	313.8	314.6	315.3	316.1	316.8
—0	301.8	302.6	303.4	304.3	305.1	305.9	306.7	307.5	308.3	309.1
+0	301.8	300.9	300.1	299.2	298.4	297.5	296.6	295.7	294.9	294.0
+10	293.1	292.2	291.3	290.4	289.5	288.6	287.6	286.7	285.7	284.8
+20	283.8	282.8	281.8	280.9	279.9	278.9	277.9	276.9	275.9	274.9
+30	273.9	272.8	271.8	270.7	269.7	268.6	267.5	266.4	265.3	264.2
+40	263.1	262.0	260.8	259.7	258.5	257.4	256.2	255.0	253.8	252.6

Appendix—Specific Heat of Saturated Ammonia Vapor

If the latent heat of vaporization and the specific heat of the saturated liquid are known as functions of the temperature, it is possible to compute the specific heat of the saturated vapor by using the general relation

$$\sigma' - \sigma = \frac{dL}{d\theta} - \frac{L}{\theta} = \theta\frac{d}{d\theta}\left(\frac{L}{\theta}\right).$$

The data for the specific heat of saturated liquid ammonia are available from a previous investigation[1] the results of which are expressed by the empirical equation

$$\sigma = 3.1365 - 0.00057\theta + \frac{16.842}{\sqrt{133 - \theta}}$$

in which σ is the specific heat in joules per g. degree at temperature θ of the saturated liquid. The rate of change $dL/d\theta$ of the heat of vaporization of ammonia with temperature and the quantity L/θ can be calculated from the results of the present work. The computed values of the specific heat σ' in joules per g. degree of saturated ammonia vapor are given in the following table:

[1] THIS JOURNAL, 40, 1 (1918).

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Temperature. °C.	Specific heat of saturated vapor. Joules/g. deg.	Temperature. °C.	Specific heat of saturated vapor. Joules/g. deg.
—45	—4.42	0	—3.54
—40	—4.29	+5	—3.48
—35	—4.17	+10	—3.43
—30	—4.05	+15	—3.40
—25	—3.95	+20	—3.36
—20	—3.85	+25	—3.34
—15	—3.76	+30	—3.33
—10	—3.68	+35	—3.33
—5	—3.61	+40	—3.34
0	—3.54	+45	—3.36

WASHINGTON, D. C.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY. No. 112.]

THE VAPOR PRESSURE OF LIQUID AMMONIA UP TO THE CRITICAL TEMPERATURE.

[PART II.]

BY FREDERICK G. KEYES AND R. B. BROWNLEE.

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CONTENTS.—1. Previous Investigations. 2. The Experimental Method and Description of the Apparatus. 3. Data and Method of Determining the Vapor Pressure as a Function of the Temperature. 4. Summary.

1. Previous Investigations.

The earliest attempt to measure the vapor pressure of liquid ammonia appears to be due to Faraday[1]. The measurements extend from —17.77 to + 28.33. At that time precise thermometry had not been developed, and, moreover, no very great precautions were taken to avoid the presence of permanent gas or other impurities soluble in liquid ammonia. The presence of permanent gas such as air in a liquid is most difficult to remove. It is in fact not possible to remove it by simply pumping away vapor or even sufficiently by freezing and pumping the vapor from the crystals.[2] The Faraday measurements, while not as accurate as may now be obtained with modern experimental facilities, are nevertheless within a few per cent. of the values obtained by Regnault.[3]

Regnault's data are given in three series of measurements each under different experimental conditions. The third series were made by means of a closed air manometer, thus requiring an accurate knowledge of the pressures corresponding to the various volumes of compressed air read from the manometer. The pressures assigned to the volume readings of the manometer were not accurately known and in consequence the ammonia

[1] Faraday, *Phil. Trans.*, **135**, 170 (1845).

[2] Young, *Phil. Mag.*, **20**, 797 (1910).

[3] Regnault, *Mem. l'Inst. France*, **26**, 598 (1847).

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vapor pressures in the third series are smaller than those given by the dynamic method used in making the observations given as Series 1 and 2. It would be of course possible to recompute the manometer readings; but the addition to the knowledge of the vapor pressure—temperature relation was thought to be too small to compensate for the labor involved, inasmuch as new measurements were to be made utilizing modern facilities. The closed air manometer measurements are ten in number extending from 10° to 80°.

There are further measurements published since Regnault's work by Blümke,[1] Brill,[2] and Davies.[3] The Blümke measurements were made from ammonia prepared from ammonia water and consist in all of four measurements from —18.5° to 63.5°. Except for the value obtained at 63.5° the values of the vapor pressure obtained are lower than the smoothed Regnault values. The pressures were read from an air manometer and use was doubtless made of the isotherms of air as determined by Amagat.[4]

The values given by Brill were obtained for the purpose of testing the form of function deduced by Nernst by the aid of the Nernst theorem, for the vapor pressure as a function of the temperature. The particular form required that the measurements be made in the temperature region where the specific volume of the saturated vapor was large compared to that of the liquid. The method employed by Brill consisted in passing air over the liquid ammonia maintained at constant temperature. The weight of ammonia in a known volume of air was then determined by passing the gas mixture into dilute acid and titrating.

The partial pressure of the ammonia was calculated by making use of the perfect gas law and Dalton's law. Evidently the accuracy of the method depends on the fulfillment of the latter laws by the mixture of air and ammonia gas. For pure ammonia gas at the saturation specific volume corresponding to —33°, the departure from the perfect gas law approaches 1%. There is no means of foretelling the deviation for an air-ammonia mixture. The most serious practical difficulty, however, in carrying out the measurement is perhaps involved in obtaining a close approximation to equilibrium in the streaming air. The measurements extend from —80.0° to —33.0°, and the boiling point under 760 mm. pressure is given as —33.1.

The measurements due to Brill are the most comprehensive in the region below the boiling point; and, in spite of the trend introduced into the results by the simplified assumptions used in calculating the data over to vapor pressures, there can be considerable confidence placed in the

[1] *Ann. Phys.*, [2] **34**, 18 (1888).
[2] *Ibid.*, [4] **21**, 170 (1906).
[3] *Proc. Roy. Soc. London*, *A* **78**, 41 (1906).
[4] *Compt. rend.*, **99**, 1153 (1884).

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pressure values corresponding to the lowest temperatures where the simple method of calculating would be most valid.

The measurements contributed by Davies were made in part for the purpose of establishing the boiling point of pure ammonia. A simple mercury manometer was used to measure the pressures and a pentane thermometer for the temperature measurements. The latter was calibrated by comparison with an air thermometer. The measurements extend from —50° to —5° and agree tolerably with the values given by Regnault's smoothed curve. There was no particular provision for precise temperature regulation of the carbon dioxide snow and alcohol bath employed by Davies. The experience of the writers has been that equilibrium between a vapor and its liquid is not quickly attained, particularly at lower temperatures. In fact it was found necessary to maintain the temperature of the thermostat at a constant value for about one-half hour, during which time the liquid was stirred or shaken, to ensure equilibrium being attained. The lag in coming to equilibrium appears to be increased as the liquid is freed more perfectly from dissolved gases. In the case of ether, for example, the liquid may be superheated 20 to 36° when very perfectly freed from dissolved air. Shaking or stirring the liquid ether, however, brings about equilibrium fairly rapidly, explosively of course if the degree of superheating has been large.

A more comprehensive discussion of the relation between the vapor-pressure measurements due to the various observers will be presented below where comparisons will be shown with the data furnished by the present investigation.

2. The Experimental Method and Description of Apparatus.

The experimental methods employed in the present work embody nothing essentially new except for certain minor details of manipulation which the particular properties of the liquid ammonia required. The ammonia used was obtained from the National Ammonia Co. of Philadelphia. A suitable quantity of the ammonia was drawn into a small steel cylinder containing metallic sodium and allowed to stand for a considerable time to ensure complete reaction of the water with the metallic sodium. The ammonia vapor from the auxiliary tank was subsequently passed into dry ammonium nitrate contained in the glass apparatus *c*, *b*, *a*, Fig. 1. This procedure made it possible to keep the ammonia at ordinary temperatures without undue pressure and permitted weighings to be made of the ammonia distilled out of the glass container. It was possible, moreover, to very completely remove dissolved gases from the ammonium nitrate-ammonia solution. The difficulty of removing with sufficient completeness the dissolved gases does not seem to be particularly emphasized in the descriptions of the methods of manipulation heretofore employed in the measurements pertaining to ammonia. The liquid appears

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to be capable of retaining considerable quantities of permanent gas. The paper by Young already referred to, makes clear the difficulty of removing gases in the case of ether. In the present work a glass bomb was used in the preliminary work and the collapsing of the vapor phase completely without rise in pressure was taken to indicate the absence of permanent gas. This method is not nearly so sensitive as the method of testing suggested by Young in his paper where use is made of an inverted bell which can be raised by means of a magnetic arrangement thereby trapping a portion of the gas phase. If the gas phase collapses under the slight hydrostatic head of liquid there can assuredly be very little gas present.

Except for a few measurements made as preliminary studies all the measurements above zero were carried out in steel containers. Two steel bombs were employed during the course of the work and they will be re-

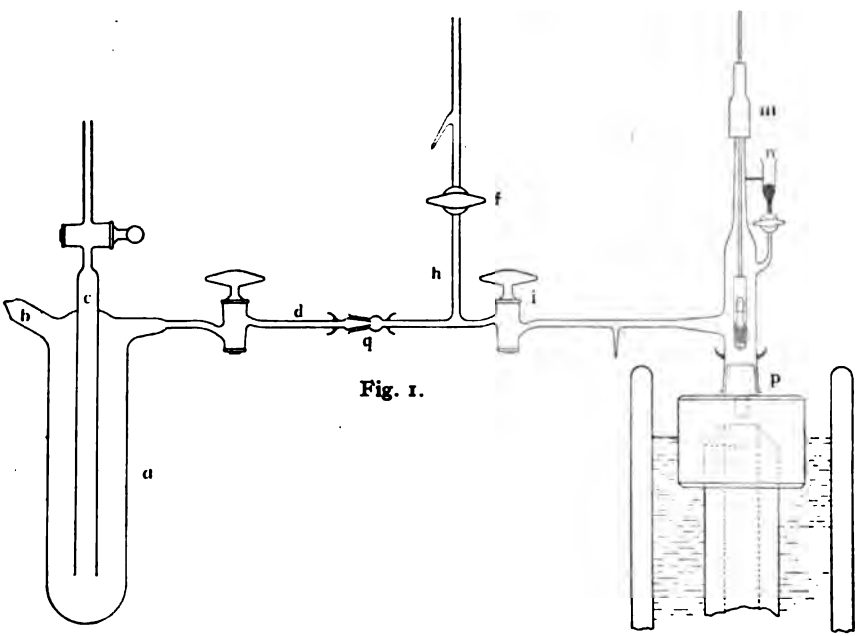

Fig. 1.

ferred to as steel bombs one and two. Steel bomb one is shown in Fig. 2 and was designed to withstand a pressure of 100 atmospheres. Steel bomb two represented partially in Fig. 1 was designed to withstand a pressure of about 1500 atmospheres. The type of the glass bombs is represented in Fig. 3 together with the method employed in making the pressure tight connection between the steel at (*a*) and the glass. The glass capillary was expanded and ground to fit the tapered steel piece after which it was cemented into place with a shellac and oil of tar composition. These joints have been used for a number of years in this laboratory and with-

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stand the pressure to the bursting limit of the glass apparatus attached by means of the joint.

The methods employed in loading the bombs are clearly shown in the figures. In the case of the glass bomb, Fig. 3, the glass portion of Fig. 1, *b*, *d*, *i*, with the exception of *m*, *n*, *p*, was sealed to the extension from *b*, Fig. 3. The ammonia container *c*, *b*, *a* was weighed and connected by means of the ground joint at *q*. The bomb and connecting tubes could be completely exhausted through *f* and after cooling the glass bomb *b* to about —38° the ammonia from *c*, *b*, *a* could be condensed to the desired amount. The bomb was finally sealed at *b* and the ammonia container *c*, *b*, *a* again weighed. The ammonia in the leads *d*, *h*, *i* was allowed for in determining the weight of ammonia contained in the bomb. The first

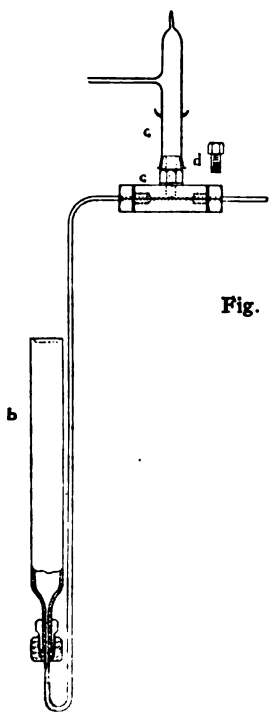

Fig. 2.

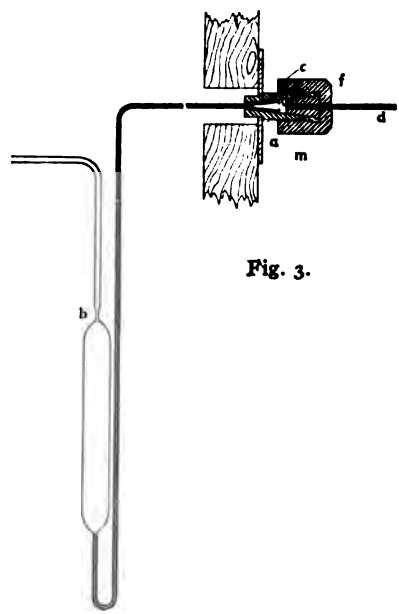

Fig. 3.

determination of the specific volumes of liquid ammonia were made in the glass bomb for which purpose the volume of the bomb had been determined to a mark on the capillary connecting tube. The data obtained, however, were later discarded in favor of specific volumes determined by a more accurate method.

The loading procedure for each of the steel bombs was different. These bombs were used for measuring the liquid and vapor isotherms as well as the vapor pressures and a definite weight of ammonia was therefore always intro-

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duced. The loading apparatus referred to in Fig. 1 was attached to *c*, Fig. 2, and after the desired quantity of ammonia had been condensed in *b* mercury was passed over from the compressor connected by means of a capillary steel tube to the right of *e*, Fig. 2. After the mercury had sealed the contents of *b* to the air, the ground glass portion *c* was removed and the locking plug *d* screwed securely into its seal. The heavier nickel steel cylinder of Fig. 1 required the locking plug to be screwed home partially by means of the wrench handle projecting through the rubber at *m*. Mercury could be flowed about the plug from *n* and thus sealed the contents of the bomb from the air until the locking plug could be securely seated. The sliding rubber connection for the temporary wrench at *m* was well covered with stopcock grease and during preliminary trials showed no leak. Of course at the moment when the wrench was manipulated ammonia at about atmospheric pressure filled the inside of the apparatus, thus preventing the entrance of air during this part of the manipulation.

The general disposition of the apparatus used to measure volume changes and pressures is shown in Fig. 4. The compressor 10, 12, 13, 14 was entirely submerged in an oil bath which kept the temperature constant to a few hundredths of a degree. The piston of the compressor was advanced by means of the screw 14 and the nut 15. The position of the piston could be read by means of the counter at 20 and the nut 15 whose periphery was divided into 100 parts thus permitting the estimation of thousandths of a turn. At 21 a riser of glass capillary was placed, use being made of the metal glass ground joint already described in connection with the glass bomb of Fig. 3. This riser had a mark several inches above the steel block 10 and the mercury was always kept at this mark by injecting oil from a pump attached to the rear face of the piston block 34. From 10 connection was made directly with the bomb about which the bath was placed. The temperature-regulated bath contained the usual heater and mercury regulator, stirrer and thermometers. The small mercury injector 38 was attached to the mercury regulator for the purpose of facilitating and reproducing settings of the regulator corresponding to specified temperatures.

The present paper deals with the vapor-pressure measurements alone, reserving for the paper dealing with the specific volumes those details concerning the use of the apparatus in measuring volume changes. It remains, however, to discuss the pressure measuring device and the calibration of the measuring piston. The piston and its cylinder were made by the Brown and Sharp Co. of Providence, R. I. Both were tempered and the piston left glass hard. After two years' use the piston showed no wear and the fit of the piston into its cylinder is so perfect that at the highest pressures employed (1000 atm.) it showed a very moderate leak. The

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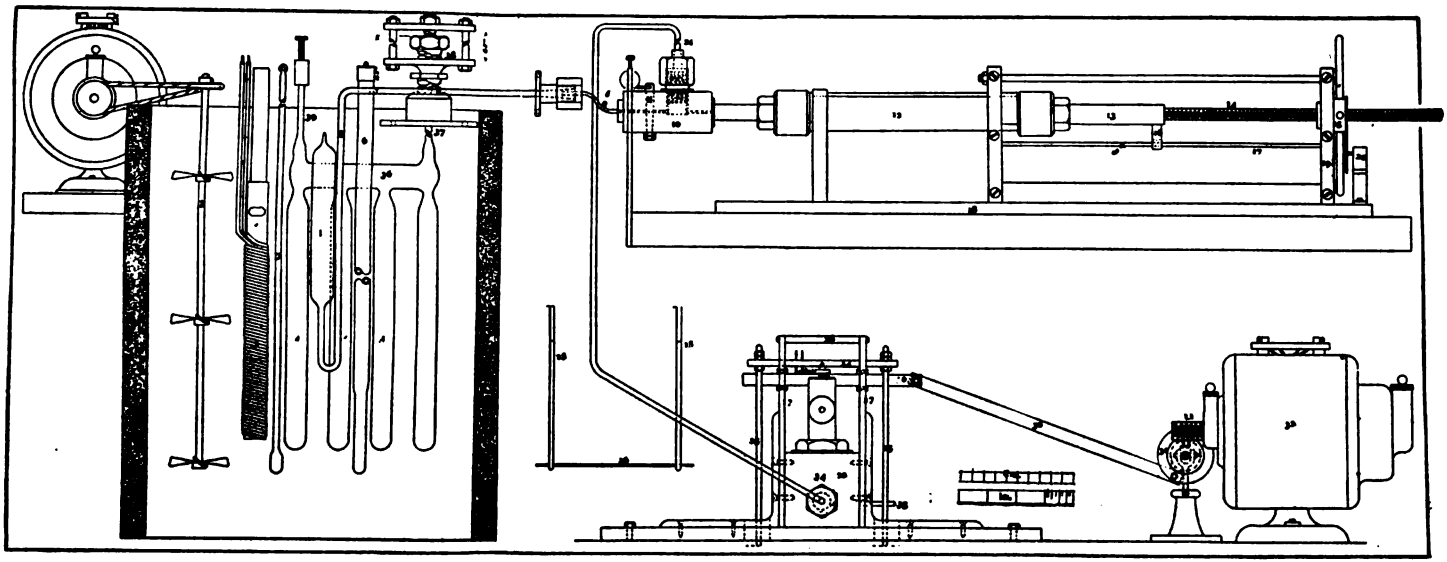

Fig. 4.

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diameter of the piston was by measurement[1] 0.47544 cm. 20°. The figure shows the means adopted to reciprocate the piston through a small angle. It is necessary to reciprocate the piston by some means to secure prompt equilibrium between the pressures within the cylinder and the equilibrating weights on the scale pan attached to 25 and 24°.

The calibration of the piston proved a most troublesome and unsatisfactory process as originally carried out. It appears that the usual practice in using the absolute pressure gage has been to observe the rise or fall of the piston due to a deficiency or excess of equilibrating weight. This, for example, was essentially the method of determining the equilibrium adopted by Holborn and Bauman[2] in their work on the vapor pressure of water. The constant of their gage or effective area was obtained by calibration against a mercury column. Four comparisons were made by means of a mercury column between 930 cm. and 1160 cm. in length. If it is assumed that the pressure is given by cw where c is a constant of the piston and w the weight on the piston area expressed in g., the constant c will vary inversely as the effective piston area. For the range of the Holborn and Bauman calibration c appeared to be constant to about one part in ten thousand.

Bridgman[3] has discussed, as completely as at present possible, the corrections due to the stresses produced by the hydrostatic pressure in a gage of the type here considered. The present elasticity theory as pointed out by Bridgman, is not sufficiently complete to enable the complete evaluation of the corrections when high pressures are to be measured. For the moderate pressures (1000 atm.) for which the present gage was designed, however, the change in the effective area of the piston due to the hydrostatic pressure is negligible.

It was discovered that the effective area, or rather the constant c of the gage, turned out in the preliminary comparisons with the mercury column to be a function of the pressure. This constant, for example at 565.2 cm. mercury height, appeared to be 4.103 while at a column height of 1238.3 cm. the constant was 4.1214, a difference of 0.52%. The study of a large number of observations disclosed the fact that as higher pressures were approached the value of c would probably approach constancy or 4.1362 at about 70 atmospheres. This resulted from employing an empirical equation which represented the "constant" as a function of the pressure accurately. The search for a more sensitive method of detecting equilibrium has established the fact that for this particular piston the method of direct visual detection of its rise or fall is not adapted for ob-

[1] The measurement was made on the large Pratt and Whitney machine of the Mechanical Engineering Department of this Institute.

[2] *Ann. Phys.*, [4] 31, 945 (1910).

[3] *Contrib. Jefferson Physical Lab.*, 6, 201 (1906).

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serving small absolute pressures and, furthermore, confirmed the conclusions of Bridgman regarding the invariability of the effective piston diameter when fluid is escaping around the piston.[1]

The method of detecting the true weight necessary to equilibrate the pressure consisted in utilizing the volume displacement of the piston due to its rise or fall to cause mercury to move in a capillary. The vertical motion of the piston was thus magnified and a telephone receiver used in connection with an induction coil secondary circuit further increased the sensitiveness with which a displacement of the capillary mercury surface could be detected.

TABLE I.

Calibration of the Pressure = Measuring Piston with Electric Contact for Determining the Equilibrium of Piston.

Mean temp. of column.	Density mercury.	Grams on piston.	Total corrected weight.	Height in feet.	Correction for oil level.	Correction for length tape. Mm.	Mm. at 0°.	Constant of piston.	Per cent. deviation from mean value 4.1351.
				Series 1.					
27.68	13.527	3035.0	3037.4	41.578	—50	—3.8	12556.0	4.1338	—0.032
26.48	13.530	1914.7	1916.5	26.291	—50	—2.3	7923.1	4.1342	—0.022
25.66	13.532	1538.2	1540.1	21.151	—50	—1.7	6365.5	4.1332	—0.046
24.87	13.534	1168.2	1169.5	16.121	—50	—1.3	4840.6	4.1390	+0.094
24.67	13.535	837.5	838.4	11.593	—50	—1.0	3467.1	4.1354	+0.007
24.37	13.536	586.4	586.9	8.190	—50	—0.7	2435.0	4.1489	huge error
23.91	13.537	410.4	410.5	5.765	—50	—0.5	1699.4	4.1399	+0.11
				Series 2.					
26.38	13.531	2627.75	3026.0	41.400	—50	—3.9	12505	4.1327	—0.058
26.38	13.531	2627.25	3025.5	41.388	—50	—3.7	12502	4.1322	—0.070
26.38	13.531	2626.00	3024.25	41.362	—50	—3.7	12494	4.1313	—0.092
26.21	13.531	1469.25	1867.31	25.620	—50	—3.2	7719	4.1338	—0.032
26.21	13.531	1467.15	1865.2	25.617	—50	—3.2	7718	4.1379	+0.068
26.21	13.531	1467.6	1865.65	25.610	—50	—3.2	1716	4.1358	+0.017
26.21	13.531	1467.4	1865.35	25.607	—50	—3.2	7715.1	4.1360	+0.022
26.21	13.531	1467.0	1865.05	25.596	—50	—3.2	7711.7	4.1348	—0.007
26.21	13.531	1464.8	1562.9	25.580	—50	—3.2	7706.9	4.1370	+0.046
26.28	13.531	646.6	1043.8	14.425	—50	—1.3	4324.7	4.1432	huge error

Density of mercury at 0°, 13.595.
Mean value of constant 4.1351 ± 0.0005.

Fig. 5 is a representation of the disposition of the apparatus during calibration against the mercury column and the same principle was made use of finally to measure the pressures throughout all the work. Referring to the diagram the gage and part of the reciprocating mechanism is shown at R. The base block into which the piston is screwed has two leads, one connecting with an oil injector, D, to supply oil lost by leakage about the piston and the other leading to the steel device A. From A the

[1] It is undoubtedly true that a piston fitting its cylinder less exactly than the one here discussed would be more suitable for direct observation.

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connection continues to the steel cylinder M which contains sufficient mercury to fill the mercury column H when oil is injected by means of the Cailletet pump, the connection to which is shown in the figure. The motion of the mercury at its junction with the oil at N in the steel capillary A was observed by means of the telephone receiver connected in series with the

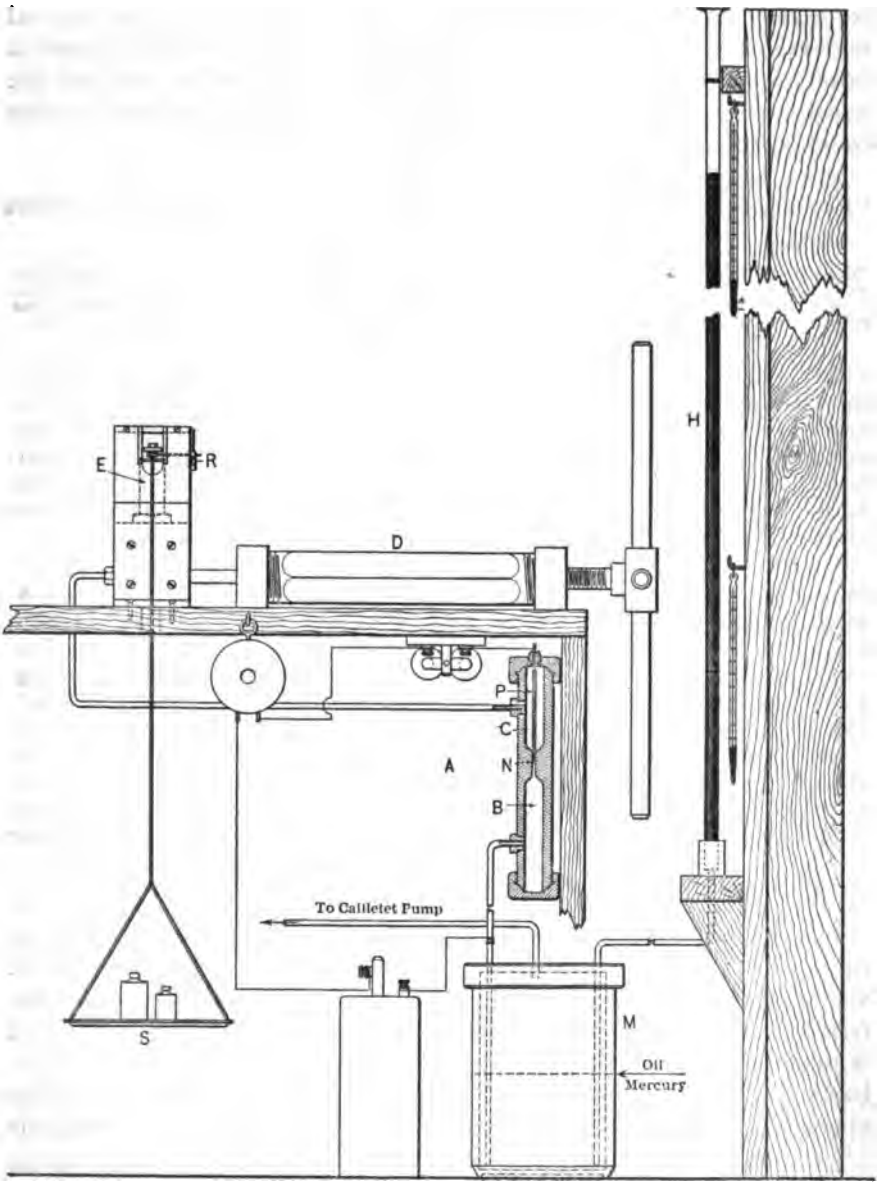

Fig. 5.

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secondary of the small induction coil as represented in the figure. An insulating joint is provided, through which passes a pointed wire. When the weights on the scale pan S are insufficient the mercury will rise in the capillary at N and excite the telephone receiver and, conversely, if in excess will break the circuit. If it is desired to verify the observation the circuit is broken by the injection of a minute quantity of oil by means of the oil injector D moving the piston to a new position. The weights could be adjusted throughout the range of the calibration so that 0.1 g. caused contact to be broken and the removal of the 0.1 g. renewed contact. Since the diameter of the capillary was about 0.15 cm. while the diameter of the piston was 0.476 it is evident that a motion of 0.01 cm. of the piston corresponds to a vertical motion of 0.1 cm. of the mercury in the capillary or a magnification of about tenfold. The diameter of the hole into which the piston fitted was only about 0.001 cm. greater that that of the piston itself and the rate of leak under the calibrating pressures amounted to but 1.2×10^{-5} cc. per minute per atmosphere and proved not sufficient to interfere with accuracy. The method has been used for all the work requiring pressure measurements in this laboratory and has greatly reduced the time required to make pressure measurements as well as increased the accuracy with which measurements could be made.

It is of course important in comparing the piston with the mercury column to determine the true mean temperature[1] of the column and this was obtained by reading the temperatures of a number of thermometers set along the column. By plotting the temperature readings as ordinates with the heights of the thermometers along the column as abscissas it is possible by graphical integration, using a planimeter, to evaluate the true mean temperature.

TABLE II.

Measurements of the Diameter of the Piston Used in Measuring Pressures.

	I.	II.	III.
Top of Piston	0.18720	0.18720	0.18720
	0.18720	0.18720	0.18720
	0.18715	0.18713	0.18713
	0.18720	0.18720	0.18720
	0.18715	0.18714	0.18715
	0.18718	0.187174	0.187176

Average diameter 0.18718 inches or 0.47544 cm. The computed constant for the pressure piston is accordingly 4.1442.

Table II shows the data obtained by measuring the diameter of the piston directly at three diameters and at five equispaced points along the

[1] It is believed now, four years after completing this work, that the chief source of error lies in controlling the temperature of the mercury column since the electrical contact method of determining equilibrium is extremely sensitive. One degree of temperature would cause a difference of one part in 5500 in the density of mercury.

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length of the piston. Each number is the mean of three settings of the electrical contact points of the measuring machine. Table III gives the calibration data obtained for the steel tape used. The comparison was made on a comparator of the Physics Department of this Institute using the department's standard meter made by the Societe Genevoise. The data show that the steel tape was 4.66 mm. too long at 51 feet or about one part in thirty-three hundred at 25°.

TABLE III.

Calibration of the Steel Tape at 25° Used in Calibrating the Pressure Piston.

Tape Reading.	Correction.	Tape Reading.	Correction.
0 to 3′	—0.54 mm.	27′–30′	—0.30
3′–6′	—0.20	30′–33′	—0.26
6′–9′	—0.18	33′–36′	—0.20
9′–12′	—0.34	36′–39′	—0.24
12′–15′	—0.20	39′–42′	—0.30
15′–18′	—0.28	42′–45′	—0.14
18′–21′	—0.34	45′–48′	—0.50
21′–24′	—0.30	48′–51′	—0.24
24′–27′	—0.10		

The density of mercury as effected by geographical position was taken into consideration in reducing the mercury heights and thus the pressures given in Table I refer to sea level at 45° of latitude and zero degrees. The weights used on the scale pan were of course calibrated. The various data of the calibration are collected in Table I.

The observations are divided into two series made at different times, and about half the observations were made independently by Mr. R. D. Mailey of this laboratory. The mean value of the constant of the gage is concordant in the two series to about one part in eight thousand. It is also evident that the constant is invariable as the height changes from about 1700 mm. to 12560 mm. or for about a sevenfold change.[1] The value of the gage constant 4.1351 mm. per g. is also seen to be in very good agreement with the extrapolated value 4.1362 obtained by the method of direct observation of the motion of the piston.

Table I shows that the method of observation by electrical contact enables a short mercury column to be used to determine the gage constant accurately. The method of direct observation of the rise or fall of the piston, on the other hand, at least in the case of the piston used in the present work, is unreliable for observing small pressures. Both methods of observation for the higher pressures (50 atm.) have been used in the

[1] The diameter of the piston by direct measurement is 0.47544 while the apparent diameter from the constant obtained by direct calibration is 0.47597. The effective diameter as pointed out by Bridgman is the mean of the diameters of the piston and hole. The diameter of the hole was, therefore, 0.00106 cm. larger than the piston. The design of the piston cylinder was not such as to permit an accurate direct measurement of the diameter of the hole.

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present paper, but the readings by the electrical contact method were much more concordant.

3. Data and Method of Determining the Vapor Pressure as a Function of the Temperature.

The preliminary vapor-pressure measurements were carried out in a glass bomb for the purpose of determining whether the ammonia distilled into the bomb from the container represented at *a*, Fig. 1 was free from permanent gases. It was found that the vapor phase collapsed promptly with no rise in pressure showing that permanent gas was absent. The measurements made in the glass apparatus were not carried to a temperature higher than 30°, however, owing to the danger of explosion. The two steel bombs used for the higher pressure work were each used to carry out two series of measurements at the higher temperatures.

All the measurements reduced from the direct observations of the vapor pressure of liquid ammonia are contained in Table IV. The temperatures at which the pressures were measured were determined in the beginning of the work by means of a mercury thermometer, but shortly after completing the measurements made in the glass apparatus use was made of a 25 ohm platinum resistance thermometer. The mercury thermometer was compared with the platinum thermometer and subsequently all mercury thermometer readings were corrected and may therefore be considered referred to the constant volume nitrogen scale. The latter temperature scale for the range of temperatures employed in the present work is of course substantially equivalent to the absolute temperature scale.

The measurements tabulated in Table IV are given in terms of mm. of mercury at 0° at 45° of latitude and sea level. They depend directly of course on the weights required to equilibrate the piston gage whose calibration has already been discussed, except for corrections due to oil and mercury levels pertaining to the apparatus in which the measurements were made. The volume of the vapor phase above the liquid throughout each of the measurements was varied from practically zero to the maximum which the apparatus permitted and each value given consequently depends on several settings of the volume piston.

For convenience in treating the data an equation expressing the logarithm of the pressure as a function of the temperature was worked out using all the measurements as given in Table IV. This equation was then used to obtain the rate of change of the vapor pressure with the temperature and the individual measurements reduced to round temperatures. The reduced measurements are collected in Table V and the concordance of the several measurements at the same temperature is thus obtained. There is included in this table a number of measurements made in a special apparatus at about the boiling point of liquid ammonia. This apparatus constructed with an electromagnetic stirrer provided effective

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TABLE IV.—EXPERIMENTAL DATA.

T. Series No. 1.	p. Soda glass bomb.
0°	3267
0	3275
0	3276
0	3285
19.90	6457
19.98	6473
20	6475
25	7545
25	7553
25	7577
25	7585
25	7681
29.85	8808
29.97	8804
29.97	8825

Series No. 2.	Soda glass bomb.
0°	3249
0	3253
0	3256
0	3261
0	3272
29.85	8763
29.85	8782

T. Series No. 1.	p. Steel bomb No. 1.
0	3153
24.64	7519
29.84	8746
34.96	10195
39.87	11697
40.37	11836
45.02	13424
49.58	15105
55.05	17400
58.77	19065
65.23	22388
69.93	24854
75.35	28090
80.10	31211
85.48	35173
90.00	38441
94.95	42353
100.51	47483

Series No. 2.	Steel bomb No. 1.
29.75	8728
29.75	8754
29.75	8755
29.75	8742
29.75	8720
29.75	8752
39.82	10102
49.86	11652
34.77	15236
44.82	13380
54.857	17336
59.91	19593
64.92	22103
70.10	24925
75.05	27888
80.14	31155
85.26	34825
90.46	38809
95.60	43035
100.84	47602

T. Series No. 1.	p. Steel bomb No. 2.
29.825	8742
29.853	8735
34.86	10126
49.83	15226

Series No. 2.	Steel bomb No. 2.
9.54	4591
20.975	6702
34.80	10142
34.80	10146
34.80	10146
34.80	10147
34.80	10147
34.90	10153
34.90	10164
34.90	10164
34.90	10168
34.90	10176
34.90	10178
44.81	13337
44.813	13382
54.88	17324
54.883	17351
64.88	22095
75.065	27880
75.197	27980
85.21	34762
85.365	34933
95.46	42887
95.651	43113
100.306	47253
104.970	51739
105.07	51743
109.87	56718
115.009	62416
115.01	62328
.....	62332
.....	62343
119.917	68173
125.00	74686
125.00	74733

stirring of the liquid under measurements and in addition the apparatus was so arranged that the vapor phase could be pumped away from time to time. It was found to be a difficult matter to secure equilibrium at the lower temperatures and this difficulty was accentuated owing to the fact that the bath surrounding the liquid ammonia could not be maintained as

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constant as desirable. A direct determination of the boiling point was therefore undertaken employing varied conditions of boiling for the purpose

TABLE V.[1]—EXPERIMENTAL DATA REDUCED TO ROUND TEMPERATURES.

	—33°.		0°.	20°.	25°.	30°.	35°.
	778.2	760.8	Mean 3255	6477.7	7545	8847.0	10206.6
	779.7	762.1	Calc. 3251	6477.1	7553	8811.8	10169.0
	786.9	758.2		6475.0	7577	8832.8	10166.7
	777.3	757.7		6492.0	7585	8802.0	10182.1
	772.9	754.7		———	7581	8821.0	10205.2
	773.2	781.5	Mean	6480.4	7602	8787.5	10204.2
	771.8	777.4	Calc.	6486.8	——	8787.5	10200.2
	773.6	779.7		Mean	7574	8773.2	10204.2
	754.4	770.5		Calc.	7584.9	8806.8	10205.2
	753.1	779.6				———	10207.1
	752.9	778.2			Mean	8808	10193.1
	747.6	782.6			Calc.	8819	10205.1
	751.9	781.2					10197.1
	764.2	778.5					10193.1
Mean	769.3						Mean 10196.0
Calc.	768.4						Calc. 10199.5

	40°.	45°.	50°.	55°.	60°.	65°.
	11739	13417	15271	17378	19645	22268
	11716	13445	15291	17399	19635	22145
	11710	13405	15293	17403	———	22158
	———	13449	———	———	Mean 19641	22177
Mean	11722.0	———	Mean 15292.0	Mean 17393.0	Calc. 19682	———
Calc.	11735.0	Mean 13429.0	Calc. 15324.0	Calc. 17380.8		Mean 22187
		Calc. 13448.0				Calc. 22167

	70°.	75°.	80°.	85°.	90°.	95°.
	24894	27872	31143	x34821	38441	x42396
	24868	27857	31060	34634	38444	42522
	———	27840	———	34608	———	42492
Mean	24881	27857	Mean 31102	34665	Mean 38443	42557
Calc.	24912	———	Calc. 31119	———	Calc. 38426	———
		Mean 27857		Mean 34640		Mean 42524
		Calc. 27854		Calc. 34593		Calc. 42600

	100°.	105°.	110°.	115°.	120°.	125°.	132.9°.
	47013	51674	56858	62321	68274	74708	Calc. 85352
	46827	51769	Calc. 56839	62406	Calc. 68223	Calc. 74489	
	46971	———		———			
	———	Mean 51769		Mean 62364			
Mean	46934	Calc. 51698		Calc. 62323			
Calc.	46954						

[1] The mean value, 3255 mm., for the vapor pressure of ammonia at 0° depends on the measurements made in the soda glass series 2. The series 1 measurements are neglected because it occurred to the writers to tap the bomb during measurements after the measurements had been completed. Those data marked *x* in the table have not been included in the mean because they seemed to be effected with a huge error. It is likely that an error was made in reading the resistance thermometer bridge resistance.

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of comparison with the manometric measurement. The apparatus was constructed with reference to a particular Beckmann thermometer which could be surrounded with beads as well as a polished platinum radiation screen, while at the bottom of the boiling vessel a small coil of wire was arranged to supply heat electrically to the liquid ammonia. The Beckmann thermometer was compared with a platinum resistance thermometer in a separate Dewar tube of sufficient size to accommodate the two instruments, at approximately the same temperature as that during the boiling-point measurement. Table VI gives the data taken and a supercooling of

TABLE VI.

Direct Determination of Boiling Point. Barometer Corrected 760.5.

Reading of current flowing through pt. spiral.	Beckmann thermometer.	Temperature corresponding to 760.5 mm.
No current	1.37	—33.13
1 amp.	1.33	...
	1.32	—33.18
	1.34 after 10 min.	—33.16
1.3 amp.	1.30	...
	1.30 after 3 min.	...
	1.30 after 2 min.	—33.20
2 amp.	1.26	—33.24
	1.26 after 2 min.	...
	1.25 after 3 min.	—33.25
4 amp. platinum wire at red heat	0.80	—33.70
	0.90	—33.60
Addition of platinum sponge:		
No current	1.37	—33.13
1 amp.	1.32	—33.18
	1.324	—33.18
	1.31	—33.19

Calibration of Beckmann with Plat. Res. Ther.

Reading Beckmann.	Temperature pt. res. therm.
1.360	—33.143
1.360	—33.141

the liquid appears to take place as more vigorous boiling is induced by means of the electrically heated wire. When particles of platinum sponge were introduced evidently no material change in the boiling temperature was produced. It is clear that the boiling point with the platinum wire at a red heat would probably dissociate the vapor to some extent, in contact, to nitrogen and hydrogen in which event the lowering of the boiling point would be accounted for. With no current passing through the wire on the other hand ebullition did not occur, while one to two amperes caused a gentle to vigorous ebullition. It seems reasonable to assume that —33.2 is very close to the normal boiling point or corrected to 760 mm. of mercury —33.21. The mean of the manometric measurements leads to —33.25, while the smoothed vapor-pressure curve, giving weight to all the higher

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pressure measurements, gives the temperature —33.22 as the normal boiling point. To compare with this value are measurements due to Brill[1] —33.1, Gibbs[2] —33.46, Perman[3] and Davies —33.5. The datum of Gibbs was taken with a pentane thermometer—an instrument not as easy to control as the thermocouple used by Brill. It should be pointed out, however, that Brill's results may be in error due to employing Dalton's law for computing the partial pressure of the amminia vapor in the air drawn over the liquid ammonia. As has been stated above there is not sufficient data available concerning pressure-volume properties of mixtures of air and ammonia to evaluate the error likely to be introduced by this assumption. At the lower temperatures the error introduced by the assumption of Dalton's law undoubtedly becomes small.

The method used to obtain an equation connecting the pressure and temperature has been described elsewhere.[4] The method has been applied in principle by H. Happel[5] and also Lionel Marks[6] and depends on finding an accurate empirical expression for a in van der Waals' formula $\log p_c/p = a(T_c/T - 1)$ where p_c and T_c are the critical pressure and the critical temperature. The values of a show a minimum when a graph is constructed with $(T_c - T)$ as abscissas. The a values were assumed capable of accurate representation by means of the series formula

$$a = a_0 + a_1 (T_c - T) + a_2 (T_c - T)^2 + \ldots + a_n (T_c - T)^n.$$

a_0 is nearly 3 and may be determined in any case by an extrapolation through $(T_c - T)$ or zero of a special graph wherein the vapor pressures near the critical point are treated. The a_0 for ammonia came out 3.02 and to avoid the minimum of the direct graph a new function, Z, was defined.

$$Z = a - a_0/T_c - T = a_1 + \ldots + a_n(T_c - T)^{n-1}.$$

The equation of Z can be easily determined and proved to be a quadratic function. The vapor-pressure formula of van der Waals written in terms of the Z function and the critical temperature becomes

$$\log p = -[Z(T_c - T)^2 + \omega]/T + m,$$

where ω is $a_0 T_c$ and m is $(\log p_c + a_0)$. This form of the vapor-pressure equation is most convenient for calculating pressures since the $Z(T_c - T)^2$ expression may be computed with sufficient accuracy by means of a slide rule. If desired the critical temperature may be absorbed in the constants of the equation.

[1] *Ann. Phys.*, [4] 21, 170 (1906).

[2] THIS JOURNAL, 27, 851 (1905).

[3] *Proc. Roy. Soc. London, A* 78, 28 (1906).

[4] "Thermodynamic Properties of Ammonia," Keyes and Brownlee, Wiley & Sons, 1916.

[5] *Ann. Phys.*, [4] 13, 340 (1904).

[6] *J. Am. Soc. Mech. Eng.*, 33, 563 (1911).

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$$\log p = -b/T + c + dT + eT^2 + \ldots.$$

The latter equation[1] is more suitable for differentiation for the purpose of computing dp/dT for use in the Clapeyron formula.

The measurements appearing in Table V have been used to prepare the graph, Fig. 6, where Z's are plotted as ordinates and (T_c —T) as abscissas. A few of Brill's law temperature measurements have been incorporated in the graph and also the boiling point calculated from the vapor-pressure equation given by Holst.[2] The data of Regnault, Brill

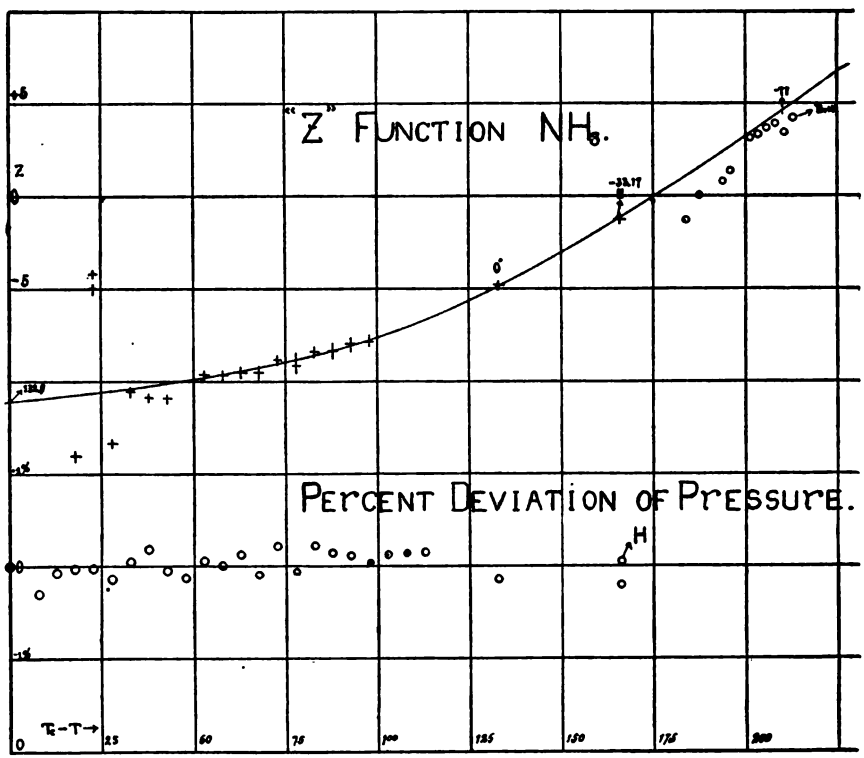

Fig. 6.

and Davies together with a few new measurements due to Holst himself were used by Holst for his formulation. The temperature at which the pressure is one atmosphere is —33.17° according to the vapor-pressure formula given by Holst.[2] The most probable value accordingly for this temperature would appear to be about —33.2. It is perceived that the line passing through the higher pressure Z values cannot be made to pass through Brill's values if —33.2 is the correct temperature for the boiling

[1] The ice point on the absolute temperature scale has been taken as 273.1°.

[2] "Les propriétés chimiques de l'ammoniaque et du chlore de méthyl," Leiden (1914).

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point. Holst has already pointed out the inconsistency of the Brill measurements as compared with the observations of Davies.

In order not to confuse the plot made from the measurements recorded in the present paper a Z plot, Fig. 7, prepared several years ago is given, showing the relation of each observer's data to the present work. This

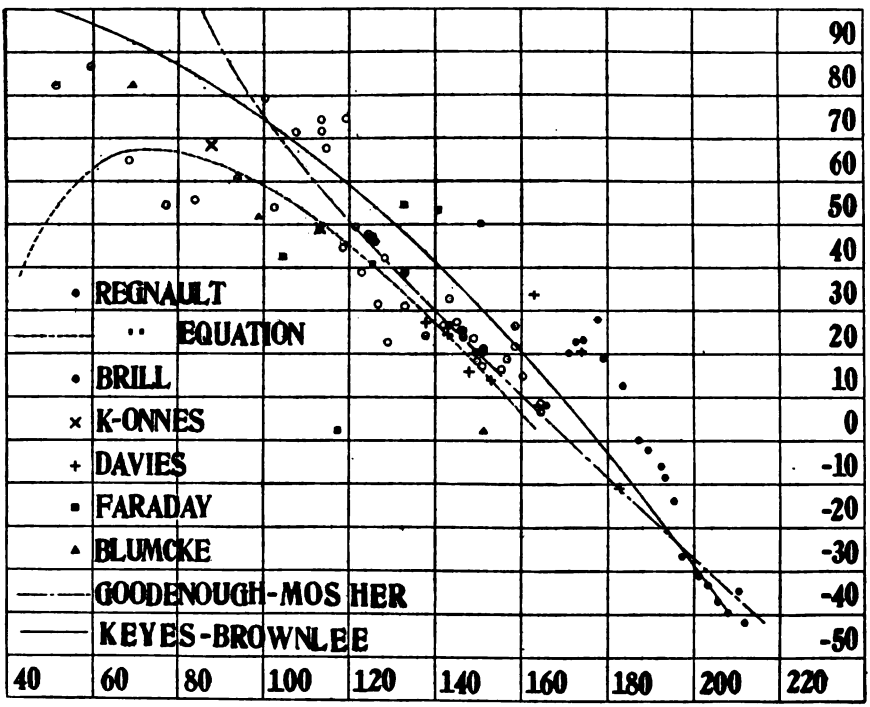

Fig. 7.

plot has drawn in it the line representing the Z equation of Fig. 6 but with different units. Since the plot is useful only as it discloses graphically differences in trend in the work of the various observers the matter of the units is immaterial. The Z equation corresponding to Fig. 6 is:

$$Z = 10^{-4}\,[-11.901 + 1.0018.10^{-2}(T_c - T) + 3.2715.10^{-4}(T_c - T)^2]$$

The vapor-pressure equations are:

$$\log_{10} p = 7.91121 - 1209.88 + Z(T_c - T)^2/T;$$

$$\log_{10} p = -1969.65/T + 16.19785 - 0.0423858\,T + 5.4131.10^{-5}\,T^2 - 3.2715.10^{-8}\,T^3.$$

The pressure units in these equations are millimeters of mercury under normal conditions while the critical temperature and pressure are taken as 132.9° and 85355 mm. or 112.3 atm.

Recently Goodenough and Mosher[1] have made a careful examination of

[1] Univ. of Ill. Expt. Station, *Bull.* 66.

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the available thermodynamic data relating to ammonia. The vapor-pressure-temperature relation was worked out with the aid of the Ramsay and Young formulas $R = R' + k(T - T')$, in which R and R′ denote the ratio of the temperatures of two different substances at two different vapor pressures, and T, T′ the absolute temperatures of one of the substances corresponding, respectively, to the pressures. Water was taken as the reference substance and all available ammonia vapor-pressure data used to obtain the constants needed for the Ramsay and Young formula. Fig. 7 shows that the Goodenough and Mosher equation gives values intermediate between those vapor pressures resulting from Regnault's smoothing of his own results and the values based on the present experimental work. Table VII gives the smoothed pressures resulting from the values of Table V together with the vapor pressures resulting from Regnault's smoothing of his own data.

TABLE VII.—FINAL COMPARISON OF PRESSURES.

Manometer.	t.	p. Calculated.	p. Observed.	p. Regnault.	%. Deviation.
Manometer.....	—33.22	760	760.8	.....	....
Boiling point.....	...	.....	759.6	.....	....
Absolute gage.....	0°	3251.0	3255.5	3183.3	—1.0
	10	4656.7	.....	4574.0	—1.78
	20	6486.8	6480	6387.8	—1.68
	25	7584.9	7574	.....	....
	30	8819.0	8808	8701.0	—1.34
	35	10199.5	10196	.....	....
	40	11735.0	11722	11595	—1.20
	45	13448.0	13429	.....	....
	50	15324.0	15292	15158	—0.92
	55	17380.8	17393	.....	....
	60	19682.0	19641	19482	—1.01
	65	22166.7	22187	.....	....
	70	24912.0	24881	24675	—0.95
	75	27853.5	27857	.....	....
	80	31119.0	31102	30843	—0.89
	85	34593.0	34640	.....	....
	90	38426.0	38443	38109	—0.83
	95	42600.0	42524	.....	....
	100	46954.0	46934	46608	—0.74
	105	51698.2	51769	.....	....
	110	56839.0	56858	.....	....
	115	62323.2	62364	.....	....
	120	68223.0	68274	.....	....
	125	74488.6	74708	.....	....
	132.9	85351.8	.....	.....	....

4. Summary.

The vapor pressures of ammonia have been measured from 0° to the critical temperature by means of the absolute piston gage. The normal boiling point has also been measured using both the manometric and dynamic

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methods. The latter method is believed to give the most accurate value for the normal boiling temperature (—33.20 ± 0.05°).

A method for examining the consistency of vapor-pressure data is used whereby it is possible to obtain easily an accurate formula connecting pressure and temperature over any desired temperature range. The equation for the vapor pressure of ammonia from the freezing point (—77) to the critical temperature (132.9) is,

$$\log_{10} p = -1969.65/T + 16.19785 - 0.0423858\,T + 5.4131.10^{-5}\,T^2 - 3.2715.10^{-8}\,T^3,$$

where the pressure units are mm. of mercury under normal conditions. The pressures given by this equation represent the experimental data within the limits of experimental error but they are the order of one per cent. higher than the values decided upon by Regnault.

An improved method of electrically determining the weight necessary to equilibrate the force due to the mercury column used in the absolute piston gage calibration is described. The electrical contact method decreases the time needed to make observations with the piston gage as well as enormously increasing the sensitiveness.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

THE VAPOR PRESSURES OF LIQUID METALS.

BY JOEL H. HILDEBRAND.

Received November 14, 1917.

A valuable paper on the vapor pressures of metals was recently published by Johnston.[1] In addition to summarizing the existing data he has calculated for each metal the constants of the vapor-pressure equation, $\log p = -A/T + B$, and the heat of vaporization, which is 4.58A. In view of the inaccuracy of much of the data involved it has seemed to the writer that it would be useful to attempt to correct these calculations by applying the rule discovered by him[2] that the entropy of vaporization (*i. e.*, the heat of vaporization divided by the temperature of vaporization on the absolute scale) is the same for all normal liquids, provided that the comparison is made at temperatures where the saturated vapors have the same concentration. It is to be noted that this differs from the familiar Trouton's Rule in that the comparison is made at temperatures of equal concentration of saturated vapor instead of at temperatures of equal vapor pressure, such as the boiling points. It has been shown that this generalization makes it possible to superimpose the vapor-pressure curve for one substance upon that for another by the aid of a

[1] Johnston, *J. Ind. Eng. Chem.*, 9, 874 (1917).

[2] THIS JOURNAL, 37, 970 (1915).

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single constant, a, which expresses the ratio of the absolute temperatures at which the two substances vaporize to give vapors of the same concentration. If the vapor pressure of the substance chosen as standard is given by the expression

$$\log p = -A_s/T + B_s,$$

then the vapor pressure of another normal substance is

$$\log p = -aA_s/T + B_s + \log a,$$

where $a = (T/T_s)_{conc.}$.

This relationship enables the vapor-pressure curve of a normal liquid to be constructed from a single point, such as the boiling point, provided we know the values of A and B for some substance we may select as standard. It seems, from the evidence in this and in the earlier paper, that the metals may be regarded as normal liquids.

Since the vapor pressure of mercury has been measured with great accuracy we will select this liquid as the standard. Using the values of Smith and Menzies,[1] and plotting $\log p$ against $1/T$ just as Johnston has done, we obtain the nearly straight line shown in the figure. The equation for this line we may take as

$$\log p = -3140/T + 7.85,$$

p being expressed in mm. of mercury. Vapor pressures of other substances, if our rule holds and the measurements are accurate, should then be given by the general equation

$$\log p = -3140\, a/T + 7.85 + \log a,$$

and the measurements should coincide with those for mercury if $\log p - \log a$ is plotted against a/T. It is easiest to determine the value of a by successive approximations. The figures show the result of this process, using data for cadmium, zinc, thallium, lead and silver.

For cadmium and zinc we have vapor-pressure measurements by Barus[2] at higher pressures and by Egerton[3] at very low pressures. These both agree with the theory, but not perfectly with each other, so that a slightly different value of a must be used in the two cases to conform with the mercury. The values for the boiling points given by Heycock and Lamplough[4] indicate that the temperatures of Barus are too high by an amount very nearly corresponding to the higher values of a used in calculating his measurements. It is very striking that the same value of a applies to the figures of Heycock and Lamplough at 760 mm. and to those of Egerton at pressures of 10^{-4} mm.

[1] Smith and Menzies, THIS JOURNAL, 32, 1447 (1910).

[2] Barus, *Phil. Mag.*, [5] 29, 141 (1890).

[3] Egerton, *Ibid.*, [5] 33, 33 (1917).

[4] Heycock and Lamplough, *Proc. Chem. Soc.*, 28, 4 (1914); *Chem. News*, 105, 66 (1912).

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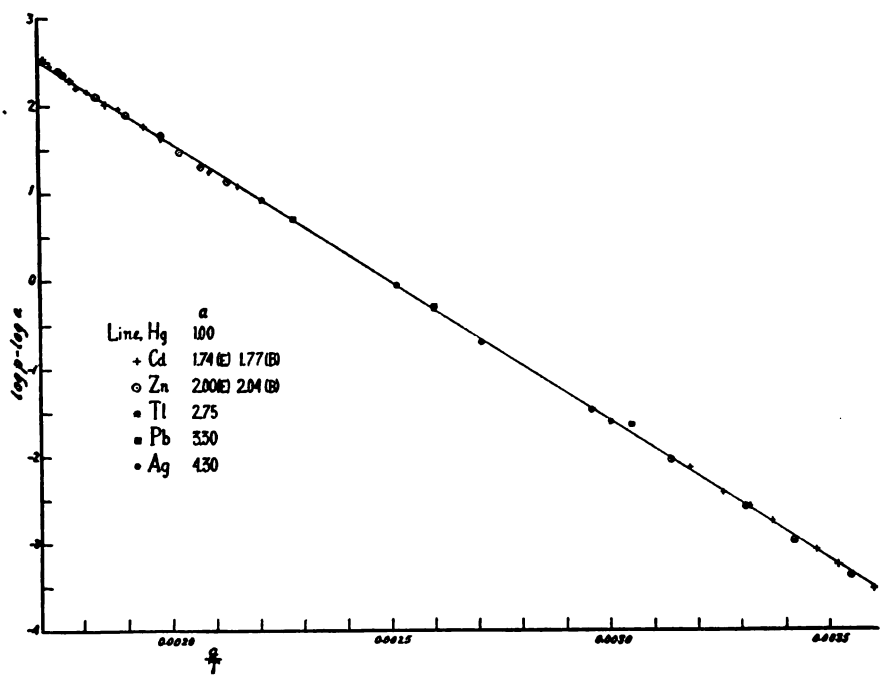
The values used for thallium, lead and silver are those measured by von Wartenberg.[1]

Table I gives the values of a for the above-mentioned elements, together with the source of the data used.

TABLE I.

Metal.	a.	Data by
Mercury	1.00	Smith and Menzies
Cadmium	1.74	Egerton; Heycock and Lamplough
	1.77	Barus
Zinc	2.00	Egerton; Heycock and Lamplough
	2.04	Barus
Thallium	2.75	von Wartenberg
Lead	3.30	von Wartenberg
Silver	4.30	von Wartenberg

These constitute practically all of the data available for testing the theory. The values for arsenic, platinum, molybdenum and tungsten, cited in Jonston's paper, apply to solid metals, and could not be expected to agree very closely with the theory which is applicable only to the vapor pressures of liquids. It is true that we have, also, a number of figures for various metals by Greenwood,[2] but, as Johnston shows, they are often inconsistent with the measurements of others, and, furthermore, do not



[1] von Wartenberg, *Z. Elektrochem.*, 19, 482 (1913).

[2] Greenwood, *Proc. Roy. Soc. London*, (*A*) 83, 483 (1910).

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lend themselves to the straight line plot to be expected in such cases. They appear, therefore, to be of little use in determining the slope of the line, and hence in fixing values of A and B. In other words, the values of A and B calculated from Greenwood's vapor pressures would vary widely, using different pairs of measurements. It seems to the writer that our theory gives a means of calculating these constants from the values of *a* necessary to bring the boiling points of these metals on to the general curve more accurately than they can be calculated by applying the Clapeyron equation to the measurements themselves. In Table II, accordingly, in addition to the values for the metals in Table I, are given values of *a* for a number of metals calculated from Greenwood's values of the boiling points at one atmosphere pressure, which may, perhaps, be considered more accurate than those at other pressures. Slightly different values would be obtained using his other points.

TABLE II.

		—A.		B.		Heat of vaporization.	
Metal.	*a*.	—3140*a*.	Johnston.	7.85 + log *a*.	Johnston.	Hildebrand.	Johnston.
Mercury.....	1.00	3140	...	7.85	..	...	...
Cadmium.....	1.74	5460	5460	8.09	8.04	25000	25000
Zinc.....	2.00	6280	6290	8.15	8.14	28800	28800
Magnesium.....	2.37	7450	7250	8.18	8.09	34100	33200
Thallium.....	2.75	8640	8850	8.29	8.50	39600	40500
Bismuth.....	2.93	9200	9010	8.32	8.12	42200	41300
Antimony.....	3.00	9430	9010	8.33	8.12	43200	41300
Lead.....	3.30	10370	9900	8.37	8.05	47500	45400
Aluminum.....	3.65	11450	11500	8.41	8.41	52500	52600
Manganese.....	3.85	12100	12300	8.44	8.55	55500	56300
Silver.....	4.30	13500	14300	8.48	8.97	61800	65500
Chromium.....	4.40	13800	14900	8.49	8.91	63200	68200
Tin.....	4.60	14450	15100	8.51	8.83	66200	69000
Copper.....	4.65	14600	16400	8.52	9.14	66900	75000
Nickel.....	4.80	15080	16700	8.53	9.12	69200	76500
Iron.....	4.90	15400	17000	8.54	9.10	70600	77800

The table gives also the values of A, of B, and of the heat of vaporization calculated from *a*, and, for comparison, the corresponding values calculated by Johnston. It will be noted that for the higher boiling metals there is a considerable difference between the two sets of values. This is due to the fact that the method of Johnston gives no certain guide as to the rate of increase of A and B, whereas the method herein described makes this a matter of linear extrapolation.

It must be emphasized that the foregoing material is in no wise to be construed as a criticism of Johnston's calculations. If the data were more accurate the well-recognized method employed by him would undoubtedly give results identical with our own. The only advantage of the new method employed herein is that it evidently furnishes a better means of criticising

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inaccurate data, and of deducing the vapor-pressure temperature function from meager data.

In conclusion, it may be stated that the theoretical bearing of the rule regarding the entropy of vaporization will be the subject of a future communication.

Summary.

The rule concerning the entropy of vaporization, previously published by the author, is shown to apply to all liquid metals for which the experimental data are trustworthy, giving a general vapor-pressure equation,

$$\log p = -3140a/T + 7.85 + \log a,$$

where a is a constant characteristic of each substance, and p is expressed in millimeters of mercury.

Values of a for metals for which we have but meager or unsatisfactory vapor-pressure data have been calculated.

These values of a permit the calculation of the heat of vaporization, and of the volatility of metals at any temperature.

BERKELEY, CAL.

[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTE OF WASHINGTON.]

THE LAWS OF CHEMICAL EQUILIBRIUM.

BY ERSKINE D. WILLIAMSON AND GEORGE W. MOREY.

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In discussing the relations which exist among the variables in chemical systems, the safest guide is the paper, now a classic, due to the genius of Willard Gibbs. Chemists in general have fought shy of it, owing to the extremely mathematical setting with which he surrounds his arguments and the result of this is that much ink has been spilled in proving, by roundabout methods, theorems which are either explicitly stated by Gibbs or are so readily deducible from his equations as to be implicit in his work. In the following pages we have attempted to popularize, insofar as such a term can be used in such a connection, the derivation of the fundamental equations and to deduce from them such extra formulas as are required for the derivation of the theorems bearing on the chemical side of equilibrium. The actual applications of the theorems will be discussed in later papers.

The greatest importance of this form of attack lies in the fact that the relations apply equally to concentrated and dilute solutions. The approximate formulas used at present for dilute solutions necessarily break down and are worse than useless as qualitative guides when examining the complicated systems which must be dealt with in geophysical problems. These approximate formulas can, however, be derived from the general ones by means of the necessary simplifying assumptions and such

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a derivation has often the advantage of emphasizing the assumptions in a manner never equaled in other methods.

Our initial discussion of equilibrium conditions is frankly inadequate but it will serve for many purposes and for those who wish real mathematical exactness nothing can hope to equal the original treatment by Gibbs.

The conditions for equilibrium are deduced from the fact that any closed system tends to reach a condition in which as much of the energy as possible has been dissipated as heat, or to be more exact, the system approaches the condition of maximum entropy consistent with its energy.[1] We can derive as many kinds of particular conditions as the kinds of energy we are considering. For example, we may have (*a*) thermal conditions regulating the flow of heat, (*b*) mechanical conditions regulating the movement of matter without change of composition, (*c*) chemical conditions regulating the changes in composition of the phases present, (*d*) electrical conditions, and so on. Usually only a few of these are used at one time, as the general equations become cumbersome when too many variables are present.

Let us consider a system at equilibrium consisting of a number of phases—vapor, solid and liquid—of various components. We shall assume that it is shut off from outside action by a rigid non-conducting envelope. This means no loss of generality, as, if the system is already in equilibrium it will still be so if enclosed in such an envelope. The following results are obtained:

I. Thermal Conditions.—The temperature must be uniform; otherwise heat will flow from high to low temperature.

II. Mechanical Conditions.—If only ordinary hydrostatic pressure is considered it must be everywhere equal, but if gravity is taken account of or membranes are present this must be modified.

III. Chemical Conditions.—The variable which determines chemical equilibrium is not so familiar as temperature, pressure or electrical potential and a few words are therefor necessary in explanation of what is best called the "chemical potential" of a substance. Consider a particular substance present in two different phases and for a moment deal with these phases separately. Let a supply of the substance be available in a reference state and an infinitesimal amount of it pass from this state to one of the phases. Keep the volume and entropy of the phase constant by sub-

[1] Gibbs' statements are as follows:

I. For the equilibrium of any isolated system it is necessary and sufficient that in all possible variations of the state of the system which do not alter its energy, the variation of the entropy shall either vanish or be negative.

II. For the equilibrium of any isolated system it is necessary and sufficient that in all possible variations in the state of the system which do not alter its entropy, the variations of its energy shall either vanish or be positive.

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tracting heat and changing the pressure. Let the energy required for the transfer be $\mu' dm$ in the case of the one phase and $\mu'' dm$ for the other, dm being the amount of substance transferred. Unless $\mu' dm$ be equal, to $\mu'' dm$, diminution of energy will take place if we let the amount dm pass in this way from the phase from which μdm is greater through the reference phase into the phase where it is less. Since this leaves the reference state unchanged, we may consider the change as merely the transfer of dm from one phase to the other. For equilibrium between the two phases, therefore, according to our hypothesis, μ' must be equal to μ''. The variable μ which bears to the mass of a component the same relation that pressure bears to volume, temperature to entropy or electric potential to quantity of electricity is what we call the "chemical potential"[1] of a substance. For equilibrium, therefore, we must have equality of chemical potentials wherever a substance occurs in different phases.

These constitute the conditions for the variables usually considered, but we can find the conditions for other variables provided we know the form of the energy terms involved.

Development of Mathematical Relations.

Since for chemical purposes we need to deal mainly with μ and the changes in μ, some necessary relations containing this variable will first be deduced. Let a phase of variable composition be subjected to slight change by having work done on it, heat added to it and its composition changed. The total energy[2] change is given by $d\epsilon = td\eta - pdv + \mu_1 dm_1 + \mu_2 dm_2 + \ldots\ldots \mu_n dm_n$, where $td\eta$ is the heat added, pdv the work done, and the other terms are the amounts of energy gained or lost in the addition or subtraction of the small amounts of the various components.

This leads as usual to

$$d(\epsilon - t\eta + pv) = -\eta dt + vdp + \mu_1 dm_1 + \ldots. + \mu_n dm_n.$$

This gives us

$$n \text{ relations like } \left(\frac{\partial \mu_r}{\partial t}\right) = -\left(\frac{\partial \eta_r}{\partial m_r}\right) = \text{spec. entropy of component } r \text{ in the phase considered.} \quad \text{(A)}$$

$$n \text{ relations like } \left(\frac{\partial \mu_r}{\partial p}\right) = \left(\frac{\partial v_r}{\partial m_r}\right) = \text{spec. vol. of comp. in this phase.} \quad \text{(B)}$$

$$\tfrac{1}{2}\, n(n-1) \text{ relations like } \left(\frac{\partial \mu_r}{\partial m_q}\right) = \left(\frac{\partial \mu_q}{\partial m_r}\right). \quad \text{(C)}$$

The subscripts are omitted as these are obviously in each case simply all the variables with the exception of the one in the denominator. These

[1] "μ" is one of the many quantities which has been called "Thermodynamic Potential" while G. N. Lewis uses the term "partial molal free energy" for it.

[2] We prefer to use Gibbs' notation for the sake of reference to his papers.

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are all valuable relations among the partial differential coefficients[1] of the variable in question. We must remember that the partial differential coefficients with respect to mass are not independent as μ depends evidently on the composition of the phase (and hence on the ratio of the masses present), not on the amount present. This can be taken account of by observing that this means that the potentials are not changed by adding to the phase more of itself, for if we add dm, etc., we get n equations of the type

$$d\mu_1 = \left(\frac{\partial \mu_1}{\partial m_1}\right) dm_1 + \left(\frac{\partial \mu_1}{\partial m_2}\right) dm_2 + \text{etc.}$$

but if $dm_1 : dm_2 : dm_3$, etc., $= m_1 : m_2 : m_3$, etc., $d\mu_1$, $d\mu_2$ and the others must vanish.

$$\therefore \quad 0 = m_1 \left(\frac{\partial \mu_1}{\partial m_1}\right) + m_2 \left(\frac{\partial \mu_1}{\partial m_2}\right) + \ldots\ldots + m_n \left(\frac{\partial \mu_1}{\partial m_n}\right).$$

$$0 = m_1 \left(\frac{\partial \mu_2}{\partial m_1}\right) + m_2 \left(\frac{\partial \mu_2}{\partial m_2}\right) + \ldots\ldots + m_n \left(\frac{\partial \mu_2}{\partial m_n}\right). \qquad \text{(D)}$$

(n such relations.)

These relations are of great importance in the applications of our equations.

Let this phase of variable composition be our reference phase and consider another phase in equilibrium with it. If this second phase is to remain in equilibrium it must undergo changes to keep the chemical potentials equal to those in the reference phase.

Therefore if $d\mu_1$, etc., be the changes in the reference phase and dm_1', dm_2', etc., be the necessary changes in the other phase to keep it in equilibrium, we must have

$$d\mu_1 = \left(\frac{\partial \mu_1'}{\partial m_1'}\right) dm_1' + \left(\frac{\partial \mu_1'}{\partial m_2'}\right) dm_2' + \ldots\ldots + \left(\frac{\partial \mu_1'}{\partial m_n'}\right) dm_n' + \left(\frac{\partial \mu_1'}{\partial p}\right) dp + \left(\frac{\partial \mu_1'}{\partial t}\right) dt$$

where the right hand symbols refer entirely to the second phase.

Similarly $d\mu_2 = \left(\frac{\partial \mu_2'}{\partial m_1'}\right) dm_1' + \left(\frac{\partial \mu_2'}{\partial m_2'}\right) dm_2' + \ldots\ldots + \left(\frac{\partial \mu_2'}{\partial m_n'}\right) dm_n' + \left(\frac{\partial \mu_2'}{\partial p}\right) dp + \left(\frac{\partial \mu_2'}{\partial t}\right) dt.$

[1] A number of these coefficients are necessarily positive. For instance all of the types A and B as all substances have positive volume and entropy. Also n of the others, namely $\left(\frac{\partial \mu_1}{\partial m_1}\right)$, $\left(\frac{\partial \mu_2}{\partial m_2}\right)$ .... $\left(\frac{\partial \mu_n}{\partial m_n}\right)$ where the increase of chemical potential of a component in respect to increase of its own concentration is considered. Going back to the definition of the quantity the reader will see that this simply states that a sub-

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$$d\mu_n = \left(\frac{\partial \mu_n'}{\partial m_1'}\right) dm_1' + \ldots\ldots + \left(\frac{\partial \mu_n'}{\partial m_n'}\right) dm_n' + \left(\frac{\partial \mu_n'}{\partial p}\right) dp + \left(\frac{\partial \mu_n'}{\partial t}\right) dt.$$

Multiplying by m_1', m_2', etc., and adding, we get

$$m_1'd\mu_1 + m_2'd\mu_2 + \ldots + m_n'd\mu_n = v'dp + \eta'dt, \qquad \text{(E)}$$

the right hand simplifying on account of relations A, B and D. This is equation number 97 in Gibbs' paper and is *one* of the convenient forms.

If the phase in equilibrium with the reference phase be a phase of fixed composition the derivation of the equation is modified slightly. Let its composition be α, β, γ, in the weight units used, etc., of the components, then

$$\mu_s dM_s = \mu_1 dm_1 + \mu_2 dm_2 + \ldots + \mu_n dm_n,$$

where $dm_1 : dm_2 : dm_3$, etc., $= \alpha : \beta : \gamma$, etc., and $\Sigma dm_1 = dM_s$.

This gives us

$$(\Sigma\alpha)\mu_s = \alpha\mu_1 + \beta\mu_2 + \text{etc.},$$

and since μ_s is a function of p and t and $(\partial\mu_s/\partial t)$ = specific volume while $-(\partial\mu_s/\partial p)$ = specific entropy by relations A and B only we get for a change in p, t and the composition of the reference phase

$$v'dp - \eta'dt = \alpha d\mu_1 + \beta d\mu_2 + \text{etc.},$$

which is of the same form as for the case of variable composition.

Condition for Non- and Meta-Stability.—If in the preceding case p and t are changed so that $\mu_s dM_s$ becomes greater than $\Sigma\mu_1 dm_1$, then the phase in question will dissolve in the reference phase. On the other hand, if it becomes less, then the phase will separate from the reference phase. In this case if the phase is not already present supersaturation may result and we have a metastable condition. This condition, by

$$vdp - \eta dt < m'_1 d\mu_1 + m'_2 d\mu_2 \ldots\ldots + m'_n d\mu_n,$$

is useful in the study of the pressure-temperature relations.

If the phase we are considering be of variable composition it is to be noted that we can only say that at least some of the components will disappear or appear, and not the whole phase, but this is generally immaterial.

Applications.—The form of equilibrium equation which we have deduced can be used to deduce the relation commonly known as the phase rule and is the most useful in tracing pressure and temperature relations in systems. Its use will be discussed at some length in the next paper on "Pressure-temperature curves in univariant systems."

For other purposes, however, it is useful to get an equation containing

stance tends to dissolve in a less concentrated and crystallize from a more concentrated solution.

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as variables the changes in composition, pressure and temperature. This could have been deduced primarily, or we can get it from Equation E by substituting for $d\mu_1$, etc.,

$$d\mu_1 = \left(\frac{\partial \mu_1}{\partial p}\right) dp + \left(\frac{\partial \mu_1}{\partial t}\right) dt + \Sigma \left(\frac{\partial \mu_1}{\partial m_1}\right) dm_1, \text{ and so on.}$$

Using our relations A and B this gives us

$$+ \Delta V dp = + \frac{\Delta H}{T} dt + \left[m_1'\left(\frac{\partial \mu_1}{\partial m_1}\right) + m_2'\left(\frac{\partial \mu_1}{\partial m_2}\right) + \text{etc.}\right] dm_1$$
$$+ \left[m_1'\left(\frac{\partial \mu_2}{\partial m_1}\right) + m_2'\left(\frac{\partial \mu_2}{\partial m_2}\right) + \text{etc.}\right] dm_2$$
$$+ \text{etc.}, \qquad (E')$$

where ΔV is the increase of volume and ΔH the heat taken in when $m_1' + m_2' +$ etc., weight units of the phase separate from a large amount of the reference phase. Referring back to the deduction of our relation D it will be seen that the coefficients of dm, etc., represent the change of the μ's for the same reaction, so the equation can be written[1]

$$+ \Delta V dp = \frac{\Delta H}{T} dt + \Sigma \Delta \mu_1 dm_1.$$

It is hardly necessary to point out that, in a one-component system where no change of composition is possible and therefore dm_1, dm_2, etc., are zero, Equation E′ simplifies to

$$\Delta V dp = \frac{\Delta H}{T} dt$$

which is the ordinary Clausius-Clapeyron relation.

In a two-component system we are generally interested in what happens at constant temperature or at constant pressure, so a simple form of equation for these cases will be found.

Along an isobar

$$-\frac{\Delta H}{T} dt = dm_1 \left[\alpha\left(\frac{\partial \mu_1}{\partial m_1}\right) + \beta\left(\frac{\partial \mu_1}{\partial m_2}\right)\right] + dm_2 \left[\alpha\left(\frac{\partial \mu_2}{\partial m_1}\right) + \beta\left(\frac{\partial \mu_2}{\partial m_2}\right)\right].$$

We can combine this with

$$dm_1 + dm_2 = 0$$

since we need only consider the composition of the reference phase and can deal with a constant weight of it.

Also from relation D

$$m_1\left(\frac{\partial \mu_1}{\partial m_1}\right) + m_2\left(\frac{\partial \mu_1}{\partial m_2}\right) = 0.$$

[1] In dealing with three-component systems Schreinemakers uses an equation which is equivalent to this form, but he uses the ratio of the components instead of their actual amounts.

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$$m_1\left(\frac{\partial\mu_2}{\partial m_1}\right) + m_2\left(\frac{\partial\mu_2}{\partial m_2}\right) = 0.$$

Simplification gives

$$-\frac{\Delta H}{T}\,dt = dm_1\left(\alpha - \frac{m_1}{m_2}\beta\right)\left(1 + \frac{m_1}{m_2}\right)\left(\frac{\partial\mu_1}{\partial m_1}\right).$$

A well-known theorem may be immediately deduced from this.

I. Let the two phases in equilibrium be a salt hydrate and solution and let dm_1 be the concentration of anhydrous salt. Consider the equilibrium curve near the point where the solution has the same composition as the hydrate. ΔH is negative, as we know of no substance which does not require heat to melt it, and the last two terms are positive. The sign of the slope of the curve therefore depends on the terms $(\alpha - m_1/m_2\,\beta)$ which is positive or negative according as α/β is greater or less than m_1/m_2, that is, whether the solution contains a greater or less proportion of water than the hydrate. Therefore the temperature increases with the concentration up to the point considered and then decreases. This can be illustrated by the solubility curves of most hydrates.

II. Let the two phases in question be a vapor and a liquid. Consider as before the point where the two phases have the same composition. The reasoning above applies except that ΔH is positive, as the vapor gives out heat in liquefying. It is impossible to say offhand whether we get a maximum or minimum temperature in this case.

Along an isotherm the equation reduces similarly to

$$\Delta V dp = dm_1\left(\alpha - \frac{m_1}{m_2}\beta\right)\left(1 + \frac{m_1}{m_2}\right)\left(\frac{\partial\mu_1}{\partial m_1}\right).$$

From this we can make deductions like those above and in particular we may mention the two known as Konowalow's Laws.[1] (1) If $\alpha/\beta = m_1/m_2$ the system has a maximum vapor pressure at the temperature in question. (2) If one component is markedly more volatile than another so that α/β is never equal to m_1/m_2, the vapor pressure increases steadily with the concentration of the more volatile component. For dilute solutions a sufficient approximation for $(\partial\mu_1/\partial m_1)$ is $[RT/(m_1 + m_2)] \times m_2/m_1$, based on the assumption of $(\partial\mu_1/\partial m_2) = -[RT/m_1 + m_2]$. This assumption is discussed by Gibbs in several places. Using this, we can get the usual forms of equations given in all text-books. However, while any one specific property such as the increase of solubility with temperature at constant pressure, or the lowering of the freezing point of a solution depends on $(\partial\mu_1/\partial m_1)$, the ratio of two will not, as the term will cancel out. This may be otherwise stated as follows: knowing the volume and heat changes involved and one relation between the concentration and another

[1] See van der Waals, "Lehrbuch der Thermodynamik."

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variable, we can in a two-component system calculate the other relations among the variables.

Theorems Regarding the Shape of Isotherms.

There are two general theorems[1] regarding tangents to isotherms which we have occasionally found useful and which can be deduced from the relations already proved and one additional one, namely—,

$$\alpha\left[\alpha\left(\frac{\partial\mu_1}{\partial m_1}\right)+\beta\left(\frac{\partial\mu_1}{\partial m_2}\right)+\ldots.+\right]+\beta\left[\alpha\left(\frac{\partial\mu_2}{\partial m_1}\right)+\beta\left(\frac{\partial\mu_2}{\partial m_2}\right)+\ldots\right]+\text{etc.}>0.$$

This can be proved as follows: Suppose we have a solid of composition α, β, etc., at a given temperature and pressure in contact with a liquid phase at the same temperature and pressure but that equilibrium is on the point of being attained so that an amount $d\mathrm{M}$ of the solid must yet dissolve so as to reach the proper equilibrium concentration. Let μ_1, μ_2, etc., be the equilibrium potentials. The potentials in the liquid will be

$$\mu_1-\left(\frac{\partial\mu_1}{\partial m_1}\right)dm_1-\left(\frac{\partial\mu_1}{\partial m_2}\right)dm_2-\text{etc.}$$

$$\mu_2-\left(\frac{\partial\mu_2}{\partial m_1}\right)dm_1-\left(\frac{\partial\mu_2}{\partial m_2}\right)dm_2-\text{etc.}$$

$$\mu_n-\left(\frac{\partial\mu_n}{\partial m_1}\right)dm_1-\left(\frac{\partial\mu_n}{dm_2}\right)dm_2-\text{etc.}$$

where $$dm_1=\frac{\alpha}{\alpha+\beta+\text{etc.}}\,d\mathrm{M}$$

$$dm_2=\frac{\beta}{\alpha+\beta+\text{etc.}}\,d\mathrm{M},\ \text{etc.}$$

But the chemical potential of the solid must be greater as it is still dissolving, and, therefore,

$$\left(\frac{\alpha}{\Sigma\alpha}\mu_1+\frac{\beta}{\Sigma\alpha}\mu_2+\text{etc.}\right)d\mathrm{M}>\left[\mu_1-\left(\frac{\partial\mu_1}{\partial m_1}\right)dm_1-\text{etc.}\right]\frac{\alpha}{\Sigma\alpha}d\mathrm{M}+\text{etc.}$$

$$\text{or}\qquad 0>\alpha\left[-\left(\frac{\partial\mu_1}{\partial m_1}\right)dm_1-\left(\frac{\partial\mu_1}{\partial m_2}\right)dm_2-\text{etc.}+\text{etc.}\right.$$

and substituting the values of dm_1, etc., we get

$$\alpha\left[\alpha\left(\frac{\partial\mu_1}{\partial m}\right)+\beta\left(\frac{\partial\mu_1}{\partial m_2}\right)+\text{etc.}\right]+\beta\left[\alpha\left(\frac{\partial\mu_2}{\partial m_1}\right)+\beta\left(\frac{\partial\mu_2}{\partial m_2}\right)+\text{etc.}\right]+\text{etc.}>0.$$

The first theorem is that if we have a solid in a three-component system in contact with a liquid phase at constant temperature and pressure the

[1] These theorems are deduced in an entirely different manner by Schreinemakers.

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variation of the composition gives us a curve which tends to surround the point representing the composition of the solid. The equation representing the equilibrium is

$$o = dm_1\left[\alpha\left(\frac{\partial\mu_1}{\partial m_1}\right)+\beta\left(\frac{\partial\mu_1}{\partial m_2}\right)+\gamma\left(\frac{\partial\mu_1}{\partial m_3}\right)\right]+dm_2\left[\alpha\left(\frac{\partial\mu_2}{\partial m_1}\right)\right.$$
$$\left.+\beta\left(\frac{\partial\mu_2}{\partial m_2}\right)+\gamma\left(\frac{\partial\mu_2}{\partial m_3}\right)\right]+dm_3\left[\alpha\left(\frac{\partial\mu_3}{\partial m_1}\right)+\beta\left(\frac{\partial\mu_3}{\partial m_2}\right)+\gamma\left(\frac{\partial\mu_3}{\partial m_3}\right)\right].$$

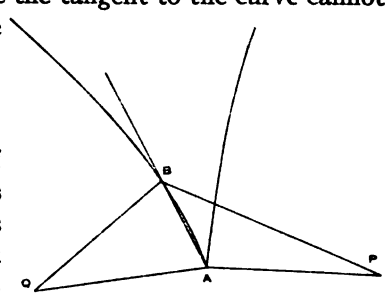
If the tangent to the curve were to pass through the point representing the solid then

$$dm_1\ dm_2\ dm_3 = (m_1-\alpha)\ (m_2-\beta)\ (m_3-\gamma),$$

hence we could have

$$o = (m_1-\alpha)\left[\alpha\left(\frac{\partial\mu_1}{\partial m_1}\right)+\beta\left(\frac{\partial\mu_1}{\partial m_2}\right)+\gamma\left(\frac{\partial\mu_1}{\partial m_3}\right)\right]+(m_2-\beta)\left[\alpha\left(\frac{\partial\mu_2}{\partial m_1}\right)\right.$$
$$\left.+\beta\left(\frac{\partial\mu_2}{\partial m_2}\right)+\gamma\left(\frac{\partial\mu_2}{\partial m_3}\right)\right]+(m_3-\beta)\left[\alpha\left(\frac{\partial\mu_3}{\partial m_1}\right)+\beta\left(\frac{\partial\mu_3}{\partial m_2}\right)+\gamma\left(\frac{\partial\mu_3}{\partial m_3}\right)\right].$$

Part of this vanishes by the relation D and the rest cannot vanish on account of the relation just proved. Hence the tangent to the curve cannot pass through the solid point and the theorem is proved.



The second theorem shows that when two curves, of the kind just considered, meet, both the tangents at the points of intersection pass between the solid points or neither does. Let the two curves meet at A in the figure and let B, a point on one of the curves, be chosen at a distance, dm_1, dm_2, dm_3 from A. Whether the points $P(\alpha, \beta, \gamma)$ and $Q(\alpha', \beta', \gamma')$ lie on the same or different sides of the curve depends on whether the ratio

$$\begin{vmatrix}\alpha & \beta & \gamma\\ m_1 & m_2 & m_3\\ dm_1 & dm_2 & dm_3\end{vmatrix} \Big/ \begin{vmatrix}\alpha' & \beta' & \gamma'\\ m_1 & m_2 & m_3\\ dm_1 & dm_2 & dm_3\end{vmatrix}$$

is positive or negative.

Let the curve considered be represented by the equation in the previous proof.

We can simplify the required ratio by multiplying the columns by the coefficients of dm_1, etc., and adding across. After canceling out common factors we get

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$$\frac{\alpha\left[\alpha\left(\frac{\partial\mu_1}{\partial m_1}\right)dm_1+\beta\left(\frac{\partial\mu_1}{\partial m_2}\right)dm_2+\gamma\left(\frac{\partial\mu_1}{\partial m_3}\right)dm_3\right]+\beta\left[\alpha\left(\frac{\partial\mu_2}{\partial m_1}\right)+\beta\left(\frac{\partial\mu_2}{\partial m_2}\right)+\gamma\left(\frac{\partial\mu_2}{\partial m_3}\right)\right]+\gamma\left[\alpha\left(\frac{\partial\mu_3}{\partial m_1}\right)+\beta\left(\frac{\partial\mu_3}{\partial m_2}\right)+\gamma\left(\frac{\partial\mu_3}{\partial m_3}\right)\right]}{\alpha'\left[\alpha\left(\frac{\partial\mu_1}{\partial m_1}\right)dm_1+\beta\left(\frac{\partial\mu_1}{\partial m_2}\right)dm_2+\gamma\left(\frac{\partial\mu_1}{\partial m_3}\right)dm_3\right]+\beta'\left[\alpha\left(\frac{\partial\mu_2}{\partial m_1}\right)+\beta\left(\frac{\partial\mu_2}{\partial m_2}\right)+\gamma\left(\frac{\partial\mu_2}{\partial m_3}\right)\right]+\gamma\left[\alpha\left(\frac{\partial\mu_3}{\partial m_1}\right)+\beta\left(\frac{\partial\mu_3}{\partial m_2}\right)+\gamma\left(\frac{\partial\mu_3}{\partial m_3}\right)\right]}.$$

The other curve yields a similar condition with the α and α' reversed. But we have just proved that the numerators are positive and the denominators, while they may have either sign, are by relation C equal, therefore the two ratios have the same sign and the theorem follows.

General Conditions for Maxima or Minima of Temperature and Pressure.

The conditions for points of maximum or minimum temperature along isobars or maximum or minimum pressure along isotherms which have already been discussed in two-component systems may be derived quite generally. If we have a system of n components we may have altogether n phases present on such a curve and therefore have $(n - 1)$ equations representing the equilibrium of each of the others with the reference phase. Let those for an isotherm be

$$\Delta V_1 dp = dm_1\left[m_1'\left(\frac{\partial\mu_1}{\partial m_1}\right)+m_2'\left(\frac{\partial\mu_1}{\partial m_2}\right)+\text{etc.}\right]+\text{etc.}$$

$$\Delta V_{n-1}\,dp = dm_1\left[m_1^{\overline{n-1}}\left(\frac{\partial\mu_1}{\partial m_1}\right)+m_2^{\overline{n-1}}\left(\frac{\partial\mu_1}{\partial m_2}\right)+\text{etc.}\right]+\text{etc.}$$

Suppose a linear relation exists such that

$$m_1 = am_1' + bm_1'' + cm_1''' + \ldots$$
$$m_2 = am_2' + bm_2'' + \ldots$$
$$m_n = am_r' + bm_n'' + \ldots$$

Multiplying the equations in order by a, b, c, etc., and adding, we get, remembering that by relation D $\Sigma m_1(\partial\mu_1/\partial m_1) = 0$.

$$(a\Delta V_1 + b\Delta V_2 + \ldots)\,dp = 0.$$
$$dp = 0.$$

That is, we have a point of maximum or minimum pressure.

In exactly the same manner we can prove for an isobar that the same condition gives us $dt = 0$, which is the condition for a maximum or minimum of temperature.

Special cases of this are as follows:

In a two-component system the condition leads us to identity in composition of two phases. For example, if we consider a salt hydrate in equi-

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librium with solution under atmospheric pressure, the maximum temperature occurs when the solution has the same composition as the hydrate, *i. e.*, when we are at the melting point of the hydrate. If the system is under its own vapor pressure instead of a constant pressure greater than the vapor pressure this deduction fails.

In a condensed three-component system such as that discussed by Rankin,[1] the theorem shows that maximum temperature points occur when the liquidus points lie on the lines joining the two solid phases present. He uses the theorem as a guide, but following Bancroft attributes it to von Alkemade, whereas it was originally proved by Gibbs by a different method from that used in the present paper.

While discussing this matter of a linear relation among the composition of our phases it should be noted that if we are neither considering an isobar nor isotherm, we deduce by the same method

$$(a\Delta V_1 + b\Delta V_2 + \ldots)\, dp = (a\Delta\eta_1 + b\Delta\eta_2 + \ldots)\, dt,$$

and hence the slope of the p-t curves is determined by the reaction among the linearly related phases. This fact is amplified and made use of in the next paper.

Any further elaboration of the equations belongs to subsequent papers where specific applications will be made. We believe that it is only along the lines laid down by Gibbs that a fruitful attack can be made on any save the outskirts of involved systems. For a comprehensive and rigorous treatment of many points, with which we have dealt hurriedly, we must again refer to his masterly paper which, it is to be hoped, will in the future be still more of an inspiration to the chemists of this country than it ever has been.

Summary.

Using Willard Gibbs' methods as a basis, general equations are developed for equilibrium in chemical systems. Special forms for simple cases are evolved and a number of more or less well-known theorems deduced from these. The application of the general equations will be considered in later papers.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION OF WASHINGTON.]

PRESSURE-TEMPERATURE CURVES IN UNIVARIANT SYSTEMS.

BY GEORGE W. MOREY AND ERSKINE D. WILLIAMSON.

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At a constant temperature a salt has a definite solubility in water, and the vapor pressure of the solution is fixed. For example, at 25°, the solu-

[1] "Lime-Alumina-Silica," *Am. J. Sci.*, 39, 1 (1915).

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bility of $Na_2SO_4.10H_2O$ in water is fixed, as is also the vapor pressure of the saturated solution. When the temperature is either raised or lowered, the solubility of $Na_2SO_4.10H_2O$ and the vapor pressure of the saturated solution both change; the first change gives rise to the solubility curve of $Na_2SO_4.10H_2O$, the second to the pressure-temperature curve, or the P-T curve, of the saturated solution.

There are several other types of P-T curves. At the transition point of $Na_2SO_4.10H_2O$,[1] the quadruple point $Na_2SO_4.10H_2O$-Na_2SO_4-solution-vapor in the binary system H_2O–Na_2SO_4, four P-T curves intersect. One of these is the P-T curve of the solutions saturated with $Na_2SO_4.10H_2O$,[2] a second, the P-T curve of solutions saturated with Na_2SO_4, a third, the dissociation pressure curve of $Na_2SO_4.10H_2O$, and the fourth, the transition point curve of $Na_2SO_4.10H_2O$, the curve which gives the change in transition point with pressure in the condensed system. It is our intention to discuss P-T curves in general, first discussing the slopes of the P-T curves at or near the invariant points, then the change in slope as we move along the curves away from the invariant point. Our discussion will be based on Gibbs' classic paper "On the equilibrium of heterogeneous substances," and especially on Equation 97 in that paper,[3]

$$vdp = \eta dt + m_1 d\mu_1 + m_2 d\mu_2 + \ldots\ldots + m_n d\mu_n, \qquad (97)$$

the fundamental equation of the phase rule. In this equation the symbols v, p, η, t represent the volume, pressure, entropy and temperature, respectively. The symbols m_1, m_2, ..., m_n, represent the masses of each of the n components, and μ_1, μ_2, ... μ_n the chemical potentials of these components, respectively.

We may generalize the above remarks in regard to the curves which intersect at the quadruple point $Na_2SO_4.10H_2O$-Na_2SO_4-L-V, as follows: At an invariant point in a system of n components, $n + 2$ phases co-exist, and the temperature, pressure and the composition of the $n + 2$ phases are determined. Addition or subtraction of heat, or increase or decrease in volume will result in a reaction taking place between the phases without change in temperature or pressure until one of the phases has disappeared. We then have $n + 1$ co-existing phases, the system is univariant, and the pressure may be expressed as function of the temperature. In his chapter, "On co-existent phases of matter," Gibbs proceeds as follows to drive an expression for the relation between the variations in pressure and temperature in a univariant system, *i. e.*, in an equilibrium between $n + 1$ phases in a system of n components. In such a case

[1] This invariant point is discussed in some detail later. See Fig. 1.

[2] For an elementary discussion of these curves see Findlay's "The Phase Rule," pp. 138, *et seq.*

[3] For a discussion of the derivation of this equation and an explanation of the terms used see the preceding paper (THIS JOURNAL, 40, 49–59 (1918)).

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we have $n + 1$ equations of the type of (97) (one for each of the co-existent phases); since the phases are co-existent the quantities p, t, and the $n\mu$'s[1] have the same value for each phase. Hence we may eliminate $d\mu_1$, $d\mu_2$, ..., $d\mu_n$ from the $n + 1$ equations. We thus obtain Gibbs' Equation 129.[2]

$$\frac{dp}{dt} = \frac{\begin{vmatrix} \eta' & m_1' & m_2' & \dots & \dots & m_n' \\ \eta'' & m_1'' & m_2'' & \dots & \dots & m_n'' \\ \eta''' & m_1''' & m_2''' & \dots & \dots & m_n''' \\ \dots & \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots \\ \eta^{n+1} & m_1^{n+1} & m_2^{n+1} & \dots & \dots & m_n^{n+1} \end{vmatrix}}{\begin{vmatrix} v' & m_1' & m_2' & \dots & \dots & m_n' \\ v'' & m_1'' & m_2'' & \dots & \dots & m_n'' \\ v''' & m_1''' & m_2''' & \dots & \dots & m_n''' \\ \dots & \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots \\ v^{n+1} & m_1^{n+1} & m_2^{n+1} & \dots & \dots & m_n^{n+1} \end{vmatrix}}.$$

This equation gives us the relation between the variations in pressure and temperature in any univariant system.

A theorem in determinants states that whenever all the terms but one in any row or column are zero,[3] the determinant reduces to the product of the term not zero and its minor. From the form of the above determinants it follows that whenever in an n-component system the composition of any phase can be expressed as a linear function of the composition of $n - 1$ or fewer phases, that is, whenever a phase reaction is possible between n or fewer phases,[4] all the composition terms relating to that phase can be reduced to zero, and the numerator and denominator of 129 reduce, respectively, to an entropy or a volume term into the same composition determinant as minor. Since the latter term occurs in both

[1] That the pressure and temperature must be the same in co-existent phases, *e. g.*, ice, water and water vapor at the triple point, is obvious. For a discussion of the necessity that the chemical potential must be the same in each phase, see the preceding paper.

[2] This equation has been put in the form of a determinant because of the great convenience of that form of notation. For those not familiar with determinants we will say that this is merely a shorthand method of indicating the familiar operation of elimination by cross multiplication. Expansion of the above determinant and elimination of $d\mu_1$, $d\mu_2$, $d\mu_3$....$d\mu_n$ from the $n + 1$ equations by cross multiplication lead to the same result.

[3] See any book on determinants; or, Mellor, "Higher Mathematics for Students of Physics and Chemistry," 2nd edition, p. 580.

[4] In a 2-component system this means that 2 phases have the same composition, *e. g.*, ice and vapor at the cryohydrate point in the system H_2O–Na_2SO_4, or two allotropic forms. In a 3-component system it means either that two phases have the same composition or that three lie in a straight line in the composition diagram.

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numerator and denominator, it cancels out, and the value of dp/dt reduces to an equation which contains only terms relating to the above reacting phases. Hence the slope of the P-T curve is independent of the presence of other phases. In other words, whenever a linear relation exists between the composition of n or fewer phases, the P-T curves of all univariant systems containing these phases coincide. When all the reacting phases have a constant composition, the curves will coincide throughout their course; when the composition of some or all of them are variable, and they only casually have such a composition that the above linear relation is possible, then the curves are tangent.[1]

Let us prove this in detail for three phases lying on a straight line in a 3-component system. Consider the P-T curves of the univariant equilibria $P' + P'' + P''' + P^{IV}$ and $P' + P'' + P''' + P^{V}$, which proceed form the quintuple point $P' + P'' + P''' + P^{IV} + P^{V}$. The equation of the first of these is

$$\frac{dp}{dt} = \frac{\begin{vmatrix} \eta' & m_1' & m_2' & m_3' \\ \eta'' & m_1'' & m_2'' & m_3'' \\ \eta''' & m_1''' & m_2''' & m_3''' \\ \eta^{IV} & m_1^{IV} & m_2^{IV} & m_3^{IV} \end{vmatrix}}{\begin{vmatrix} v' & m_1' & m_2' & m_3' \\ v'' & m_1'' & m_2'' & m_3'' \\ v''' & m_1''' & m_2''' & m_3''' \\ v^{IV} & m_1^{IV} & m_2^{IV} & m_3^{IV} \end{vmatrix}}.$$

Now assume that P', P'', P''' lie on a straight line in the composition diagram.[2] We then have the relation

$$A'P' = A''P'' + A'''P'''$$

and hence also

$$A'm_1' = A''m_1'' + A'''m_1'''$$
$$A'm_2' = A''m_2'' + A'''m_2'''$$

and

$$A'm_3' = A''m_3'' + A'''m_3'''$$

By substituting these values of m_1', m_2', m_3' in the above determinants, and subtracting A'' times the second row and A''' times the third row from A' times the first row, we get

$$\frac{dp}{dt} = \frac{\begin{vmatrix} A'\eta' - A''\eta'' - A'''\eta''' & 0 & 0 & 0 \\ \eta'' & m_1'' & m_2'' & m_3'' \\ \eta''' & m_1''' & m_2''' & m_3''' \\ \eta^{IV} & m_1^{IV} & m_2^{IV} & m_3^{IV} \end{vmatrix}}{\begin{vmatrix} A'v' - A''v'' - A'''v''' & 0 & 0 & 0 \\ v'' & m_1'' & m_2'' & m_3'' \\ v''' & m_1''' & m_2''' & m_3''' \\ v^{IV} & m_1^{IV} & m_2^{IV} & m_3^{IV} \end{vmatrix}}$$

[1] Schreinemakers (*Proc. Acad. Sci. Amsterdam*, 19, 514–27, and subsequent papers

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which reduces to

$$\frac{dp}{dt} = \frac{A'\eta' - A''\eta'' - A'''\eta''' \begin{vmatrix} m_1'' & m_2'' & m_3'' \\ m_1''' & m_2''' & m_3''' \\ m_1^{IV} & m_2^{IV} & m_3^{IV} \end{vmatrix}}{A'v' - A''v'' - A'''v''' \begin{vmatrix} m_1'' & m_2'' & m_3'' \\ m_1''' & m_2''' & m_3''' \\ m_1^{IV} & m_2^{IV} & m_3^{IV} \end{vmatrix}}$$

Similarly, the relation between the variations of P and T in the second of the above univariant equilibria $P' + P'' + P''' + P^V$, reduces to the same expression. It will be observed that, since the coefficients A', A'', A''' are those which occur in the reaction equation[1]

$$A'P' = A''P'' + A'''P'''$$

the numerator in the expression

$$\frac{dp}{dt} = \frac{A'\eta' - A''\eta'' - A'''\eta'''}{A'v' - A''v'' - A'''v'''} = \frac{\Delta\eta}{\Delta v},$$

is the entropy change[2] taking place in the reaction, the denominator, the volume change. Hence we see that whenever three phases lie on a straight line in the composition diagram the P-T curves of all ternary equilibria containing these three phases coincide with each other and with the P-T curve of the univariant binary equilibrium between the three phases alone.

As will be explained later, from this theorem alone we are able from a knowledge of the composition of the phases at an invariant point, but without any knowledge of the volume or entropy changes, to deduce the order of the slopes[3] of the $n + 2$ P-T curves which proceed from an invariant point. These curves will extend on both directions from the invariant point; in one direction the equilibrium under consideration will be stable, in the other direction, metastable. To tell the actual position of any curve, or to distinguish between the stable and metastable portions of any one curve, a knowledge of the volume and entropy changes is necessary. However, it will be shown that two adjoining curves, *i. e.*,

in the same Journal) mentions some special cases of this general theorem.

[2] An example of this is found in Fig. 3, there the phases being $K_2Si_2O_5.H_2O$, $K_2Si_2O_5$ and vapor, the vapor phase containing only H_2O, and its composition being represented by the apex of the component triangle.

[1] The actual values of these coefficients are deduced and discussed below, in the discussion of the change in slope with change in composition of a phase of variable composition.

[2] It will be remembered that the entropy η is defined by the $d\eta = dQ/T$, where Q is the heat change taking place at the absolute temperature T. Hence for η we may substitute Q/T or L/T, where L is the change in latent heat.

[3] By "the order of the slopes of the P-T curves" is meant the sequence in which we will cut the curves as we circle around the invariant point; reversing the direction of rotation reverses the sequence but does not affect the order.

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curves which are not separated by either the stable or metastable portions of other curves, *e. g.*, the P-T curves of the univariant ternary equilibria $P' + P'' + P''' + P^{IV}$ and $P' + P'' + P''' + P^{V}$, will coincide in their stable portions, that is, are stable in the same direction from the invariant point, when the phases P^{IV} and P^{V} lie on opposite sides of the straight line $P'P'''$, and *vice versa*. Examples of this are discussed later. Similar relations are found in systems containing any other number of components. In a 2-component system the univariant equilibrium consists of three phases. When the phases P' and P'' in the univariant equilibria $P' + P'' + P'''$ and $P' + P'' + P^{IV}$ have the same composition, the P-T curves of these equilibria are stable in the opposite direction when the phases P''' and P^{IV} lie on the same side of the point $P'P''$. An example of this is found in the cryohydrate point ice-$Na_2SO_4.10H_2O$-L-V in the binary system H_2O–Na_2SO_4. Here the vapor phase consists of H_2O only; ice and vapor have the same composition. In the concentration diagram, the phases $Na_2SO_4.10H_2O$ and solution lie on the same side of the point representing the composition of both ice and vapor, hence the curves ice + vapor + $Na_2SO_4.10H_2O$ and ice + vapor + solution will coincide, stable to metastable. That such is the case is well known.[1] Also in a system of four components when the phases P', P'', P''' and P^{IV} lie on a plane the curves $P' + P'' + P''' + P^{IV} + P^{V}$ and $P' + P'' + P''' + P^{IV} + P^{VI}$ are stable in the same direction when the phases P^{V} and P^{VI} lie on opposite sides of the plane $P'P''P'''P^{IV}$. The same principle may be extended to systems of any number of components. We will now prove the general theorem.

In the preceding paper[2] it was shown that equality of the chemical potential μ is a necessary condition for chemical equilibrium, and that if the chemical potential of a substance in one given phase is greater than the chemical potential of the same substance in another phase, the two phases are not in equilibrium in regard to that substance, which will tend to pass from the phase in which its chemical potential is the greater into the phase in which its chemical potential is the lesser. At the triple point ice-water-steam in the one-component system H_2O, the chemical potential of H_2O in all three phases is the same. If we simultaneously change the pressure and temperature so as to proceed along any one of the three P-T curves which intersect at the triple point, one of the phases will disappear. By giving these changes we have given greater increments to the chemical potential of the phase which disappears than to the chemical potentials of the other two phases; the chemical potential of water remains equal in these two phases since we, by

[1] See Findlay's "The Phase Rule," p. 128.

[2] THIS JOURNAL, 40, 49–50 (1918).

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hypothesis, have given such changes of pressure and temperature as to proceed along the P-T curve of stable coincidence of these phases.

The fundamental equations of the form of (97) for the three phases which co-exist at the triple point are

$$v^v dp = \eta^v dp + m^v d\mu^v$$
$$v^l dp = \eta^l dt + m^l d\mu^l$$
$$v^s dp = \eta^s dt + m^s d\mu^s$$

in which the exponents v, l, s refer to the vapor, liquid and solid phases. Each of these equations may be divided by the mass m of the phase; in the resulting equations

$$v^v dp = \eta^v dt + d\mu^v$$
$$v^l dp = \eta^l dt + d\mu^l$$
$$v^s dp = \eta^s dt + d\mu^s$$

the volume and entropy terms refer to the specific volume and entropy of each phase.

Now if, as stated above, we proceed along the P-T curve of the condensed system ice + liquid, one of the P-T curves which intersect at the triple point, we can obtain a value for $d\mu$, the change in the chemical potential, from the two equations of the type of (97) referring to the liquid and solid phases by solving the two equations for dt in terms of dp, which will give us

$$dt = \frac{v^l - v^s}{\eta^l - \eta^s} dp,$$

and substituting this value of dt in one of the original equations. Substituting in the equation referring to the liquid phase, we get

$$d\mu = v^l - \mu^l \frac{v^l - v^s}{\eta^l - \eta^s} dp.$$

Similarly, the value of $d\mu^v$ for the same increments, *i. e.*, along the same curve, is given by

$$d\mu^v = v^v - \eta^v \frac{v^l - v^s}{\eta^l - \eta^s} dp.$$

Now, since we have, by hypothesis, proceeded along the stable portion of the curve ice + liquid,

$$d\mu^v > d\mu.$$

Hence

$$dp\left[\left(v^v - \eta^v \frac{v^l - v^s}{\eta^l - \eta^s}\right) - \left(v^l - \eta^l \frac{v^l - \eta^s}{\eta^l - \eta^s}\right)\right] > 0,$$

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which reduces to

$$\frac{dp[(v^v - v^l)(\eta^l - \eta^s) - (v^l - v^s)(\eta^v - \eta^l)]}{\eta^l - \eta^s} > 0,$$

one form of the condition for stability of the equilibrium solid + liquid.

When we consider the actual magnitude of the various terms in this equation we see that the coefficient of dp in the numerator is necessarily positive. All the individual terms $(v^v - v^l)$, $(\eta^v - {}^s\eta)$, $(\eta^v - \eta^l)$ and $(v^l - v^s)$ are of necessity positive except the last one, the volume change of melting of ice, which is negative. But the last term is affected by the negative sign, hence the term as a whole is positive, and the coefficient of dp has a positive sign.[1] The equilibrium in question will then be stable as the pressure is increased from the invariant point when the denominator is positive; $(\eta^l - \eta^s)$ is of necessity positive, hence the equilibrium ice + liquid is stable with increasing pressure from the invariant point; on decreasing the pressure we pass on to the metastable portion of the curve, into a region where vapor is stable.

By solving for dp in the above equations of the type of (97) referring to the solid and liquid phases, we get an exactly similar inequality,

$$\frac{dt[(v^v - v^l)(\eta^l - \eta^s) - (v^l - v^s)(\eta^v - \eta^l)]}{v^l - v^s} > 0$$

which gives the condition for stability with change in temperature. It will be observed that the condition for temperature stability differs from the condition for pressure stability in having dt in place of dp in the numerator, and in having the volume change $(v^l - v^s)$ in place of the entropy change. Since the coefficient in the numerator is unchanged, it is always positive; the equilibrium solid + liquid is stable with increasing temperature when the denominator is positive, and is stable with decreasing temperature when the denominator is negative. In the exceptional case of H_2O, this volume change is negative, hence the equilibrium ice + liquid is stable with decreasing temperature from the triple point; on increasing the temperature we pass on to the metastable portion of the curve, into a region in which vapor is stable.

The above reasoning may be generalized as follows: At an invariant point, if we give the variables increments satisfying the $(n + 1)$ equations of the type of (97) for the univariant equilibrium, $P' + \ldots + P''' + P^{IV} + \ldots P^{n+1} + P^{n+2}$ (in which phase P'' is missing), we will move

[1] The case that $(v^l - v^s)$ is negative is, of course, exceptional. But in any case, the coefficient of dp is positive, since the two entropy changes are of the same order of magnitude, while the volume change on evaporation is many times larger than the volume change on melting.

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along the P-T curve of this equilibrium. In one direction from the invariant point the missing phase P'' will be stable, in the other direction phase P'' will be unstable. In the first case, we will be on the metastable prolongation of the P-T curve, in the second case, we will be on the stable portion of the P-T curve.

In the preceding paper the condition that a given phase is unstable, the condition that in the one-component system discussed above was given by its chemical potential becoming greater than the chemical potential of the stable co-existing set of phases, is given by the inequality

$$vdp - \eta dt > m_1 d\mu_1 + m_2 d\mu_2 + \ldots + m_n d\mu_n.$$

The condition that the equilibrium

$$P' + \ldots + P'' + P^{IV} + \ldots + P^{n+1} + P^{n+2}$$

is stable is that the missing phase P'' is unstable. By solving the $(n + 1)$ equations of the type of (97) referring to the $(n + 1)$ co-existing phases of this equilibrium for $d\mu_1$, $d\mu_3$, $d\mu_4$, and dt in terms of dp and substituting in the above inequality (the quantities v, η, m_1, m_3, $\ldots$ m_n referring to phase P'') the condition for stability takes the following form:

$$dp \frac{\begin{vmatrix} \eta' & v' & m_1' & m_2' & m_3' & \ldots & \ldots & m_n' \\ \eta'' & v'' & m_1'' & m_2'' & m_3'' & \ldots & \ldots & m_n'' \\ \eta''' & v''' & m_1''' & m_2''' & m_3''' & \ldots & \ldots & m_n''' \\ \eta^{IV} & v^{IV} & m_1^{IV} & m_2^{IV} & m_3^{IV} & \ldots & \ldots & m_n^{IV} \\ \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots \\ \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots \\ \eta^{n+1} & v^{n+1} & m_1^{n+1} & m_2^{n+1} & m_3^{n+1} & \ldots & \ldots & m_n^{n+1} \\ \eta^{n+2} & v^{n+2} & m_1^{n+2} & m_2^{n+2} & m_3^{n+2} & \ldots & \ldots & m_n^{n+2} \end{vmatrix}}{\begin{vmatrix} \eta' & m_1' & m_2' & m_3' & \ldots & \ldots & m_n' \\ \eta''' & m_1''' & m_2''' & m_3''' & \ldots & \ldots & m_n''' \\ \eta^{IV} & m_1^{IV} & m_2^{IV} & m_3^{IV} & \ldots & \ldots & m_n^{IV} \\ \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots \\ \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots \\ \eta^{n+1} & m_1^{n+1} & m_2^{n+1} & m_3^{n+1} & \ldots & \ldots & m_n^{n+1} \\ \eta^{n+2} & m_1^{n+2} & m_2^{n+2} & m_3^{n+2} & \ldots & \ldots & m_n^{n+2} \end{vmatrix}} < 0^1 \quad (1)$$

The equilibrium $P' + \ldots + P''' + P^{IV} + \ldots\ldots P^{n+1} + P^{n+2}$ will be stable if this expression is negative, and *vice versa*. Also the univariant equilibrium $P'' + P''' + \ldots P^{n+1} + P^{n+2}$ is stable when the expression

[1] This inequality applies to pressure changes; the expression referring to temperature changes is exactly similar, and the subsequent reasoning applies to either.

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$$dp \frac{\begin{vmatrix} \eta' & v' & m_1' & m_2' & m_3' & \dots & \dots & m_n' \\ \eta'' & v'' & m_1'' & m_2'' & m_3'' & \dots & \dots & m_n'' \\ \eta''' & v''' & m_1''' & m_2''' & m_3''' & \dots & \dots & m_n''' \\ \eta^{IV} & v^{IV} & m_1^{IV} & m_2^{IV} & m_3^{IV} & \dots & \dots & m_n^{IV} \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ \eta^{n+1} & v^{n+1} & m_1^{n+1} & m_2^{n+1} & m_3^{n+1} & \dots & \dots & m_n^{n+1} \\ \eta^{n+2} & v^{n+2} & m_1^{n+2} & m_2^{n+2} & m_3^{n+2} & \dots & \dots & m_n^{n+2} \end{vmatrix}}{\begin{vmatrix} n'' & m_1'' & m_2'' & m_3'' & \dots & \dots & m_n'' \\ n''' & m_1''' & m_2''' & m_3''' & \dots & \dots & m_n''' \\ n^{IV} & m_1^{IV} & m_2^{IV} & m_3^{IV} & \dots & \dots & m_n^{IV} \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ n^{n+1} & m_1^{n+1} & m_2^{n+1} & m_3^{n+1} & \dots & \dots & m_n^{n+1} \\ n^{n+2} & m_1^{n+2} & m_2^{n+2} & m_3^{n+2} & \dots & \dots & m_n^{n+2} \end{vmatrix}} < 0 \qquad (2)$$

is negative. It will be observed that this latter quantity is affected by a negative sign.

The numerators of the two expressions given above are identical. When a linear relation exists between the phases $P''', P^{IV}, \dots P^{n+1}, P^{n+2}$, the denominators reduce to

$$\Delta\eta \begin{vmatrix} m_1' & m_2' & m_3' & \dots & \dots & m_n' \\ m_1''' & m_2''' & m_3''' & \dots & \dots & m_n''' \\ \dots & \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots \\ m_1^{n+1} & m_2^{n+1} & m_3^{n+1} & \dots & \dots & m_n^{n+1} \\ m_1^{n+2} & m_2^{n+2} & m_3^{n+2} & \dots & \dots & m_n^{n+2} \end{vmatrix} \qquad (3)$$

and

$$\Delta\eta \begin{vmatrix} m_1'' & m_2'' & m_3'' & \dots & \dots & m_n'' \\ m_1''' & m_2''' & m_3''' & \dots & \dots & m_n''' \\ \dots & \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots \\ m_1^{n+1} & m_2^{n+1} & m_3^{n+1} & \dots & \dots & m_n^{n+1} \\ m_1^{n+2} & m_2^{n+2} & m_3^{n+2} & \dots & \dots & m_n^{n+2} \end{vmatrix} \qquad (4)$$

in which $\Delta\eta$ denotes the entropy change which takes place when these n phases, $P_3, P_4, \dots P^{n+1}, P^{n+2}$, react.

It will be observed that these two expressions are identical except for the first row of the determinants, which in (3) contains the composition terms of phase P', and in (4) contains the composition terms of phase P''. Hence it is evident that the numerical values of expressions 1 and 2 will be the same, *i. e.*, the two curves will be stable in the same direction from the invariant point, when (3) and (4) have opposite signs

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(since (1) and (2) have opposite signs). But (3) and (4) will have opposite signs only when phases P' and P'' lie on opposite sides of the onefold P''', P^{IV}, ..., P^{n+1}, P^{n+2}. In a 2-component system this onefold is a point; in a 3-component system, a line; in a 4-component system, a plane, etc.

The above may be summarized as follows: When two adjoining P-T curves, which represent the relation between the variations in pressure and temperature in two different univariant equilibria between $n + 1$ phases in a system of n components, coincide, due to a linear relation being possible between the compositions of the n phases common to both equilibria, *i. e.*, to these n phases lying on the onefold n, whose position is determined by the above linear relation, these equilibria are stable in the same direction from the invariant point, *i. e.*, their stable portions coincide, when the other two phases lie on opposite sides of the onefold n. By "the other two phases" is meant the phases, one in each of the univariant equilibria, which do not lie on the onefold n. In a 2-component system, the onefold n is a point; in a 3-component system, a line; in a 4-component system, a plane, etc.

The above has been proved for the case that a linear relation exists between the compositions of n of the $n + 2$ phases which co-exist at the invariant point. The cases that a linear relation exists between the composition of $n - 1$, $n - 2$, ... $n - a$, phases may be regarded as a special case of the above.

The actual number of coincidences possible is an interesting question. If among the $(n + 2)$ phases at an invariant point a phase reaction is possible between $(n - a)$ phases, then there are $(a + 2)$ phases which play no part in the reaction. The following P-T curves will then coincide: (1) the P-T curve of the univariant equilibrium between the $(n - a)$ phases in the system of $[(n - a) - 1]$ components; (2) the P-T curves of the various univariant equilibria containing the $(n - a)$ phases, together with each of the $(a + 2)$ other phases in the various systems of $(n - a)$ components; (3) the P-T curves of the various univariant equilibria containing the $(n - a)$ phases, together with every possible pair of the $(a + 2)$ other phases in the various systems of $[(n - a) + 1]$ components; (4) the P-T curves of the various univariant equilibria containing the $(n - a)$ phases together with every possible triplet of the $(a + 2)$ other phases in the various systems of $[(n - a) + 2]$ components, etc., until the system of n components is reached. The coincidences will be stable or metastable according to whether the number of phases on each side of the onefold $n - a$ are both odd or even, or are odd on one side, even on the other.

As an example of the above, consider the P-T curves which intersect at the cryohydrate point in a system of four-components, H_2O and the 3 non-volatile salts S_1, S_2 and S_3, which do not form hydrates. Here the two

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phases ice and vapor have the same composition; $a = 2$ and $(n - a) = 2$ phases have the same composition; the other $(a + 2) = 4$ phases have different compositions, and play no part in the reaction. The following curves will coincide:

(1) The P-T curve of the equilibrium between the $(n - a) = 2$ phases ice + V in the system of $(n - a) - 1 = 1$ component. One curve, the curve ice + V.

(2) The P-T curves of the equilibria between the $(n - a) = 2$ phases, ice + V, together with each, separately, of the $(a + 2) = 4$ other phases in the system of $(n - a) = 2$ components. Four curves: ice + V + L, ice + V + S_1, ice + V + S_2, ice + V + S_3. The last three of these will coincide stably with each other, metastably with the first, and all will coincide with the curve (ice + V).

(3) The P-T curves of the equilibria between the $(n - a) = 2$ phases, ice + V, together with every possible pair of the $(a + 2) = 4$ other phases in the various systems of $[(n - a) + 1] = 3$ components. Six curves: ice + V + L + S_1, ice + V + L + S_2, ice + V + L + S_3, ice + V + S_1 + S_2, ice + V + S_1 + S_3, ice + V + S_2 + S_3. The first three curves will coincide stably with each other, metastably with the last three.

(4) The P-T curves of the equilibria between the $(n - a) = 2$ phases ice + V, together with every possible triplet of the $(a + 2) = 4$ other phases in the systems of $[(n - a) + 2] = 4$ components. Four curves: ice + V + L + S_1 + S_2, ice + V + L + S_1 + S_3, ice + V + L + S_2 + S_3, ice + V + S_1 + S_2 + S_3. The first three curves will coincide stably with each other, metastably with the fourth. There are a total of 15 curves which coincide, representing one unary, four binary, six ternary, and four quaternary univariant equilibria.

Before illustrating the application of the above principles to actual cases, we will point out certain generalizations which may be made concerning the P-T curves from the state of aggregation of the phases. The actual value of dp/dt for any univariant equilibrium is given by Equation 129, which, as will be shown later, is equivalent to

$$\frac{dp}{dt} = \frac{\Delta\eta}{\Delta v}$$

in which $\Delta\eta$ is the entropy change, Δv the volume change of the reaction in question. Whenever we have a reaction in which the vapor does not take part, *e. g.*, the reaction

$$S' + S''' = S'' + L$$

the slope of the P-T curve is always very great, because of the small value of Δv. In other words, the P-T curves of all condensed systems are almost vertical, and go from the invariant point to regions of higher pressure,

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and in almost all cases, higher temperature. When the reaction is one between solid phases and vapor, *e. g.*, the dissociation pressure curve of S′,

$$S' = S'' + v.$$

The P-T curve always goes from the invariant point to regions of lower temperature and pressure; since Δv is large (except under high pressure), the slope of the curve is comparatively small. In reactions of the type

$$S' + L = S'' + V$$

in which both liquid and vapor take part, dp/dt may be large or small, positive or negative. We will consider this case in detail later.

We will now consider the application of the above principles to the determination of the sequence of P-T curves around an invariant point.[1] The method used is based on the fact that the order of the slopes dp/dt of the various curves is determined by the masses of the phases which take part in the various univariant reactions. This is evident from Gibbs' Equation 129, or from the expanded form of 129 given below. The method of application of this criterion is by considering what curves will coincide when we vary the composition of different phases. If by varying the composition of one phase in a certain direction n phases get on the one-fold (n), then, as proved above, the P-T curves of the two univariant equilibria formed by these n phases with each of the other two phases will coincide; these two curves must be adjoining curves, and no other curves can be between them. By repeating this reasoning, assuming the composition of the same phase to change in other directions, or assuming the composition of another phase to change, the relative positions of the P-T curves, the order in which they succeed one another around the invariant point, can be deduced. The stable and metastable portions can be distinguished by means of the theorems previously given.

First consider a simple case, the curves at the quadruple point $Na_2SO_4.10H_2O$-Na_2SO_4-L-V in the binary system H_2O–Na_2SO_4. The Na_2SO_4 content of these phases increases in the order V < L < $Na_2SO_4.10H_2O$ < Na_2SO_4; this is indicated in Fig. 1. The P-T curve of the condensed system L + $Na_2SO_4.10H_2O$ + Na_2SO_4 is practically vertical, going to regions of higher pressure; the dissociation-pressure curve, the curve V + $Na_2SO_4.10H_2O$ + Na_2SO_4, goes to lower temperatures and lower pressures. They are so drawn in Fig. 1. Now, if the two solid phases were to coincide in composition, these two curves would coincide, metastably, since the phases V and L lie on the same side of the two solid phases. Hence there

[1] The question of the sequence of P-T curves around an invariant point has been discussed by Smits (*Proc. Acad. Sci. Amsterdam*, **18**, 800–804 (1916)), and by Schreinemakers, "Die Heterogenen Gleichgewicht," 1, and, in more detail, in the series of papers in "In-, mono-, and divariant equilibria" in *Proc. Acad. Sci. Amsterdam*, beginning with **18**, 116–26 (1916). The treatment in this paper is from a totally different point of view.

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can be no other curves in between these two. Now, if the liquid were to have the same composition as $Na_2SO_4.10H_2O$, the curves $Na_2SO_4.10H_2O$ + L + V and $Na_2SO_4.10H_2O$ + Na_2SO_4 + L would coincide, stable to stable. But, since there can be no curve between the two curves $Na_2SO_4.10H_2O$ + Na_2SO_4 + L and $Na_2SO_4.10H_2O$ + Na_2SO_4 + V, the curve $Na_2SO_4.10H_2O$ + L + V must lie between the curves $Na_2SO_4.10H_2O$ + Na_2SO_4 + L and $Na_2SO_4.10H_2O$ + V; otherwise it could not coincide with the former curves. Also, if V and L were to have the same composition, the curves $Na_2SO_4.10H_2O$ + L + V and Na_2SO_4 + L + V would coincide, stable to metastable. Hence the metastable portion of curve Na_2SO_4 + L + V must lie between the curve $Na_2SO_4.10H_2O$ + L + V and either the curve $Na_2SO_4.10H_2O$ + Na_2SO_4 + V or the curve $Na_2SO_4.10H_2O$ + Na_2SO_4 + V. But it cannot be in the former position, because, as we have just seen, no curves may lie between the curves $Na_2SO_4.10H_2O$ + L + V and $Na_2SO_4.10H_2O$ + Na_2SO_4 + L. Hence the metastable portion of curve Na_2SO_4 + L + V must lie between the stable portions of curves $Na_2SO_4.10H_2O$ + L + V. and $Na_2SO_4.10H_2O$ + Na_2SO_4 + V, as drawn in Fig. 1.

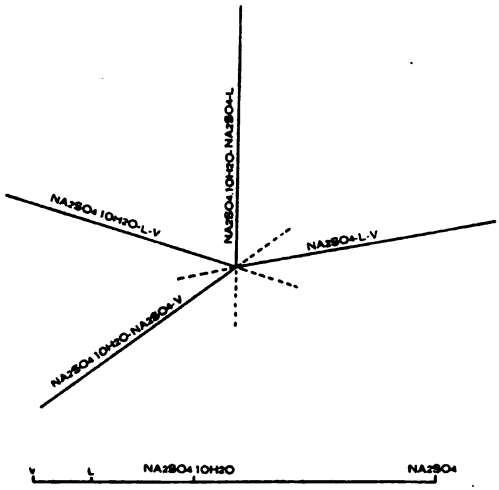

Fig. 1.—The sequence of P-T curves at the quadruple point V-L-$Na_2SO_4.10H_2O$-Na_2SO_4.

Now consider a three-component system, and assume that the phases

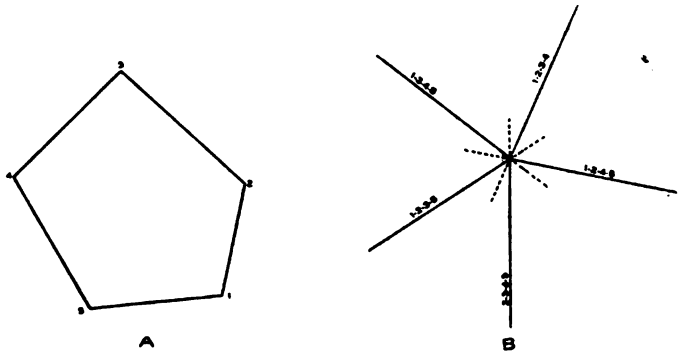

Fig. 2.—The sequence of P-T curves around a quintuple point. The compositions of the five phases are shown in Fig. 2A; the sequence of P-T curves in Fig. 2B.

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have the compositions shown in Fig. 2A. If the composition of phase P'' were to change so that phases P', P'' and P''' lay on a straight line, then the curves $P' + P'' + P''' + P^{IV}$ and $P' + P'' + P''' + P^{V}$ would coincide; stable to metastable, since phases P^{IV} and P^{V} are on the same side of the line $P'P''P'''$. Draw them in any arbitrary position, as shown in Fig. 2B. Now, if phase P''' were to change in composition so that phases P'', P''' and P^{IV} lay on a straight line, curves $P' + P'' + P''' + P^{IV}$ and $P'' + P''' + P^{IV} + P^{V}$ would coincide, stable to metastable. Hence these curves must lie as drawn in Fig. 2B; no curve may lie between these two curves. If phase P^{IV} were to get on the line $P'''P^{V}$, curves $P' + P''' + P^{IV} + P^{V}$ and $P'' + P''' + P^{IV} + P^{V}$ would coincide metastably; curve $P' + P''' + P^{IV} + P^{V}$ must lie as shown, and no curve may lie between these two curves. Similarly, curve $P' + P'' + P^{IV} + P^{V}$ must lie between the metastable portions of curves $P' + P'' + P''' + P^{V}$ and $P' + P''' + P^{IV} + P^{V}$.

Let us see under what conditions the stable parts of curves $P' + P'' + P''' + P^{IV}$ and $P' + P'' + P^{IV} + P^{V}$ can coincide. For such a coincidence to take place, phase P'' would have to change its composition until it lay on the line $P'P^{IV}$. Before it could do this, it would just get on, then cross, the line $P'P'''$ (Fig. 2A); this would cause curves $P'P''P'''P^{IV}$ and $P'P''P'''P^{V}$ to coincide, metastably, then change places. There then would be no curves between the stable portions of $P' + P'' + P^{IV} + P^{V}$ and $P' + P''' + P^{IV} + P^{V}$; as phase P'' approached the line $P'P^{V}$, these two curves would get closer to each other, and would coincide in their stable portions when phase P'' got on the line $P'P^{IV}$.

The same method may be extended to systems of more components. In the case of quaternary systems, as stated before, the onefold n is a plane, etc.

Let us apply the above considerations to the quintuple points in the ternary system H_2O–K_2SiO_3–SiO_2, and pay particular attention to the question of the sequence of the P-T curves around the invariant (quintuple) point. For the purpose of this discussion, we will combine the above theorems in regard to the conditions under which P-T curves coincide and in regard to the factors which determine whether the curves coincide stable to stable or stable to metastable in the following rule: Whenever in a ternary system three phases lie on a straight line, the P-T curves of all the ternary univariant equilibria containing these three phases coincide with each other and with the P-T curve of the univariant binary equilibrium between the three phases alone. When the other two phases at the quintuple point lie on the same side of the line on which lie the compositions of the three reacting phases, the curves coincide stable to metastable; when the other two phases lie on opposite sides of the line

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on which lie the composition of the three reacting phases, the curves coincide stable to stable.

The composition of all the phases which are met with in the ternary system H_2O–K_2SiO_3–SiO_2 are shown in Fig. 3.[1] The points indicating the composition of the solid phases are indicated. In treating this system we will assume that the vapor phase contains H_2O only. The presence of K_2O in the vapor has been detected,[2] but the amount was very small. The boundary curves show the change in composition of the liquid phase

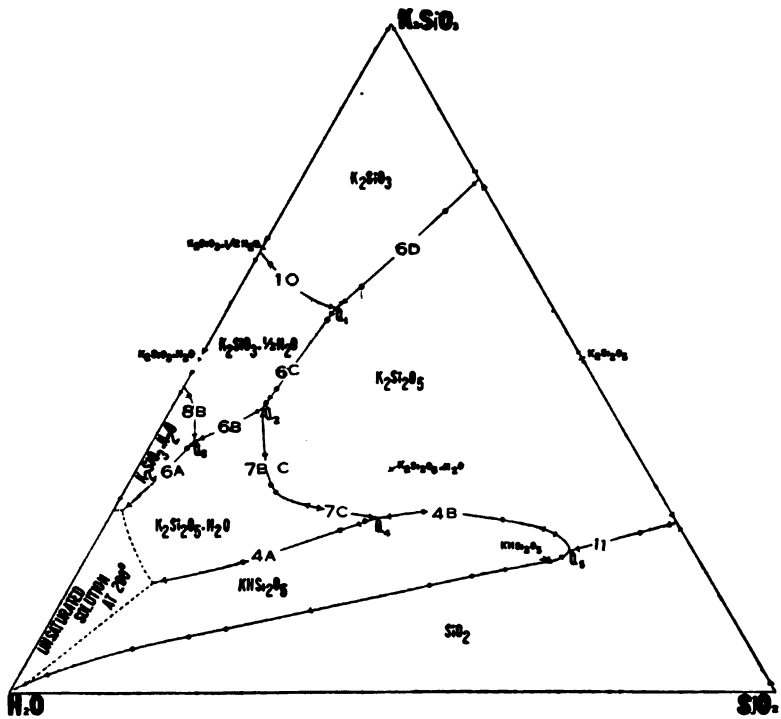

Fig. 3.—The boundary curves in the ternary system H_2O–K_2SiO_3–SiO_2. The compound stable in contact with liquid and vapor in each field is shown by the large letters; the point representing the composition of the compound, by the small letters. Arrows show the direction of falling temperature. The broken line is the isotherm at 200°. For explanation of the numbers on the curves, see the legend to Fig. 5.

in the univariant equilibria $S' + S'' + L + V$ as we pass from quintuple point to quintuple point or from quintuple point to quadruple point in the limiting binary systems. The composition of the liquid phase at each quintuple point is given by the point of intersection of three boundary curves; these points are designated by the letters Q_1, Q_2, etc. The P-T

[1] For a detailed account of the experimental study of this system, see Morey and Fenner, THIS JOURNAL. 39, 1173–1229 (1917). Figs. 3 and 4 are copied from there.

[2] Consult the discussion of this point on p. 1210 of the above paper.

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curves experimentally determined are shown in Fig. 4. Fig. 5 is a diagrammatic representation of the P-T curves, which is easier to follow.

At quintuple point Q_1 we have the 3 solid phases K_2SiO_3, $K_2SiO_3.0.5H_2O$ and K_2SiO_3, the liquid phase whose composition is given by the point Q_1, and the vapor phase, whose composition is given by the H_2O apex of the component triangle (Fig. 3). Since K_2SiO_3, $K_2SiO_3.0.5H_2O$ and V lie on a straight line, the curves $K_2Si_2O_5 + K_2SiO_3 + K_2SiO_3.0.5H_2O + V$ (curve 10*a*)[1] and $K_2SiO_3 + K_2SiO_3.0.5H_2O + L + V$ (curve 10*b*) will coincide; metastably, since the phases $K_2Si_2O_5$ and L lie on the same side of the line V-K_2SiO_3. These two curves also coincide with the dissociation-pressure curve of $K_2SiO_3.0.5H_2O$ in the binary system H_2O–K_2SiO_3 (curve 10*a* + 10*b*), Fig. 5, hence their position is as shown.

If the composition of the phases were such that V, L, and $K_2Si_2O_5$ lay on a straight line, the P-T curves of the univariant equilibrium $K_2SiO_3 + K_2Si_2O_5 + L + V$ (curve 6*d*) would coincide, metastably, with the P-T curve $K_2SiO_3.0.5H_2O + K_2Si_2O_5 + L + V$ (curve 6*c*); if the phases V, L, K_2SiO_3 lay on a straight line, the curve $K_2SiO_3 + K_2Si_2O_5 + L + V$ (curve 6*d*) would coincide, stably, with the curve $K_2SiO_3 + K_2SiO_3.0.5H_2O$

[1] The curves are numbered as in Figs. 3, 4 and 5. In Fig. 3 only curves of the type S′ + S″ + L + V are shown. In Fig. 5 the P-T curves of the condensed systems are not numbered; their position is obvious.

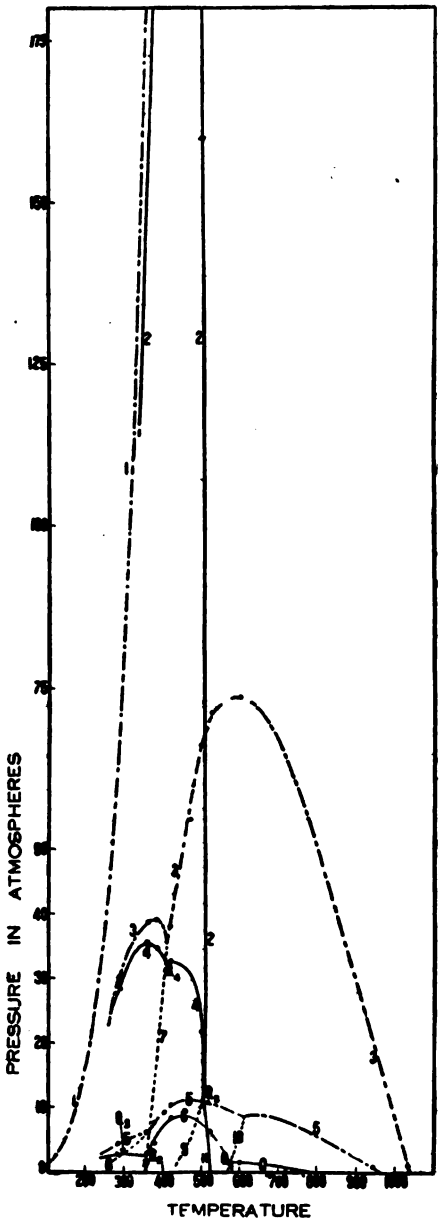

Fig. 4.—The P-T curves for the various univariant systems. The dot-dash curves represent binary systems; the full curves, the ternary univariant systems 2 solids–L–V; the dotted curves, the dissociation-pressure curves, the equilibria 3 solids–V. For explanation of the numbers on the curves, see the legend to Fig. 5.

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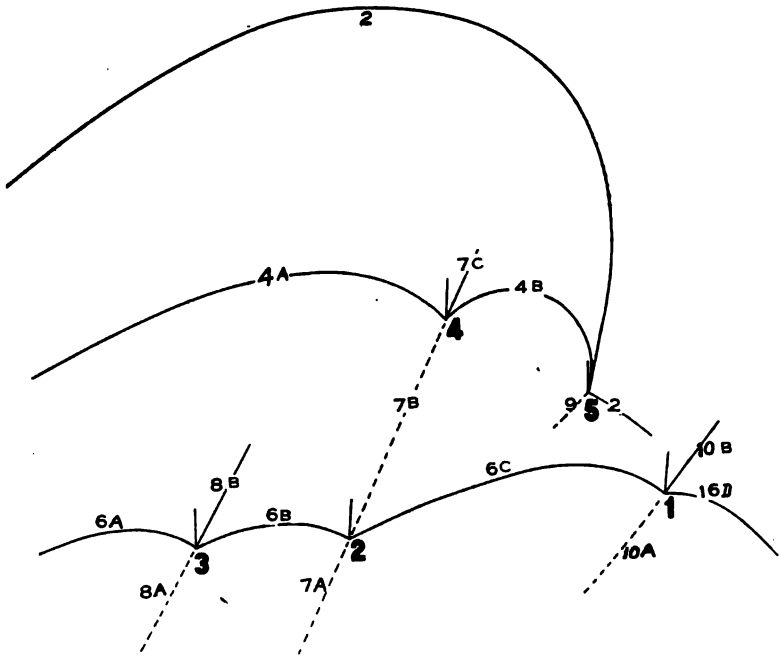

Fig. 5.—A diagrammatic representation of the ternary univariant equilibria shown in Fig. 4. Similar curves in Figs. 3, 4, and 5 are numbered the same. Following is a list of the phases stable along each curve:

Curve 2 $KHSi_2O_5 + SiO_2 + L + V$.
" 4*a* $K_2Si_2O_5.H_2O + KHSi_2O_5 + L + V$.
" 4*b* $K_2Si_2O_5 + KHSi_2O_5 + L + V$.
" 6*a* $K_2SiO_3.H_2O + K_2Si_2O_5.H_2O + L + V$.
" 6*b* $K_2SiO_3.{}^1/_2H_2O + K_2Si_2O_5.H_2O + L + V$.
" 6*c* $K_2SiO_3.{}^1/_2H_2O + K_2Si_2O_5 + L + V$.
" 6*d* $K_2SiO_3 + K_2Si_2O_5 + L + V$.
" 7*a* $K_2Si_2O_5.H_2O + K_2Si_2O_5 + K_2SiO_3.{}^1/_2H_2O + V$.
" 7*a* + 7*b* $K_2Si_2O_5.H_2O + K_2Si_2O_5 + KHSi_2O_5 + L + V$.
" 7*b* + 7*c* $K_2Si_2O_5.H_2O + K_2Si_2O_5 + L + V$.
(7*b* + 7*c* together, Curves Q_2Q_4, from Q_2 to the quadruple point $K_2Si_2O_5 + K_2Si_2O_5.H_2O + L + V$ in binary system (Fig. 3); Curve 7*c* alone, Curve Q_2Q_4 from quadruple point to Q_4.)
" 7*a* + 7*b* + 7*c* $K_2Si_2O_5.H_2O + K_2Si_2O_5 + V$ (binary system H_2O–$K_2Si_2O_5$).
" 8*a* $K_2SiO_3.H_2O + K_2SiO_3.{}^1/_2H_2O + K_2Si_2O_5.H_2O + V$.
" 8*b* $K_2SiO_3.H_2O + K_2SiO_3.{}^1/_2H_2O + L + V$.
" 8*a* + 8*b* $K_2SiO_3.H_2O + K_2SiO_3.{}^1/_2H_2O + V$ (binary system H_2O–K_2SiO_3).
" 9 $KHSi_2O_5 + K_2Si_2O_5 + SiO_2 + V$.
" 10*a* $K_2SiO_3.{}^1/_2H_2O + K_2SiO_3 + K_2Si_2O_5 + V$.
" 10*b* $K_2SiO_3.{}^1/_2H_2O + K_2SiO_3 + L + V$.
" 10*a* + 10*b* $K_2SiO_3.{}^1/_2H_2O + K_2SiO_3 + V$ (binary system H_2O–K_2SiO_3).
" 11 $K_2Si_2O_5 + SiO_2 + L + V$.

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+ L + V (curve 10*b*). Hence curve $K_2SiO_3 + K_2Si_2O_5 + L + V$ (6*d*) must lie between the metastable prolongation of curve $K_2SiO_3.0.5H_2O + K_2Si_2O_5 + L + V$ (6*c*) and the stable portion of $K_2SiO_3 + K_2SiO_3.0.5H_2O + L + V$ (10*b*). The position of the latter curve being fixed, the position of the curves $K_2SiO_3 + K_2Si_2O_5 + L + V$ (6*d*) and $K_2SiO_3.0.5H_2O + K_2Si_2O_5 + L + V$ (6*c*) must either be as shown at Q_1, Fig. 5, or the position of these curves in regard to the curves $K_2Si_2O_5 + K_2SiO_3 + K_2SiO_3.0.5H_2O + V$ (10*a*) and $K_2SiO_3 + K_2SiO_3.0.5H_2O + L + V$ (10*b*) must be reversed. That the latter arrangement cannot be correct is shown by the fact that if $K_2SiO_3.0.5H_2O$ - L - $K_2Si_2O_5$ were on a straight line, the curve $K_2SiO_3.0.5H_2O + K_2Si_2O_5 + L + V$ (6*c*) would coincide with the curve $K_2SiO_3 + K_2SiO_3.0.5H_2O + K_2Si_2O_5 + L$, the P-T curve of the condensed system. But such a coincidence is possible only with the arrangement shown in Fig. 3; the reversed arrangement cannot be the correct one.

In order to show further the relation between the composition diagram and the P-T diagram, let us consider under what conditions the curves $K_2SiO_3 + K_2SiO_3.0.5H_2O + K_2Si_2O_5 + L$ (the P-T curves of the condensed system) and $K_2SiO_3 + K_2Si_2O_5 + L + V$ (6*d*) will coincide stably. For this coincidence to take place, it is necessary that the phases L, K_2SiO_3 and $K_2Si_2O_5$ lie on a straight line in the composition diagram (Fig. 3), which intersects internally the line V-$K_2SiO_3.0.5H_2O$. On reference to Fig. 3 we see that before the phases can take on the position mentioned above, it will be necessary for the phases K_2SiO_3, $K_2SiO_3.0.5H_2O$ and $K_2Si_2O_5$, then the phases V, L and K_2SiO_3, to fall on straight lines. But in the P-T diagram, the first of these will result in the curves $K_2SiO_3 + K_2SiO_3.0.5H_2O + K_2Si_2O_5 + L$ and $K_2SiO_3 + K_2SiO_3.0.5H_2O + K_2Si_2O_5 + V$ (10*a*) approaching each other, coinciding, then again diverging, having changed places. Similarly, as a result of the second triplet of phases getting on a straight line, the curves $K_2SiO_3 + K_2Si_2O_5 + L + V$ (6*d*) and $K_2SiO_3 + K_2SiO_3.0.5H_2O + L + V$ (10*a*) will change places. The curves $K_2SiO_3 + K_2SiO_3.0.5H_2O + K_2Si_2O_5 + L$ and $K_2SiO_3 + K_2Si_2O_5 + L + V$ (6*d*) now lie next to each other, their stable portions adjoining, and when the phases L, K_2SiO_3 and $K_2Si_2O_5$ fall on a straight line these two curves will coincide in their stable portions.

The quintuple point Q_3 is exactly similar to Q_1; instead of $K_2SiO_3.0.5H_2O$, K_2SiO_3 and $K_2Si_2O_5$ we have $K_2SiO_3.H_2O$, $K_2SiO_3.0.5H_2O$ and $K_2Si_2O_5.H_2O$, respectively. Making these substitutions, the discussion of Q_1 will apply to Q_3.

Quintuple points Q_2 and Q_4 also are similar to each other. Both contain the same three phases V, $K_2Si_2O_5.H_2O$ and $K_2Si_2O_5$. At Q_2 we also have the liquid represented by the point Q_2 and the solid phase $K_2SiO_3.$-

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$0.5H_2O$; at Q_4 we have the liquid represented by the point Q_4 and the solid phase $KHSi_2O_5$. Since in both systems the phases V, $K_2Si_2O_5.H_2O$ and $K_2Si_2O_5$ lie on a straight line, the curve V + $K_2Si_2O_5.H_2O$ + $K_2Si_2O_5$ + $K_2SiO_3.0.5H_2O$ (7*a*), which proceeds from Q_2 to lower temperatures and pressures, and the curve V + $K_2Si_2O_5.H_2O$ + $K_2Si_2O_5$ + $KHSi_2O_5$ (7*b* + 7*a*), which proceeds from Q_4 to lower temperature and pressure, and the curve V + L + $K_2Si_2O_5.H_2O$ + $K_2Si_2O_5$ (7*b* + 7*c*), which proceeds from both Q_2 and Q_4 to higher temperatures and pressures, coincide with each other and with the dissociation-pressure curve of $K_2Si_2O_5.H_2O$ in the binary system H_2O–$K_2Si_2O_5$ (curve 7*a* + 7*b* + 7*c*). The position of the other curves which proceed from Q_2 and Q_4 are easily found by the same mode of reasoning as that applied to the curves at Q_1.

The quintuple point Q_5 differs from the others in the system in the fact that the liquid phase Q_5 lies inside the triangle $K_2Si_2O_5$-SiO_2-$KHSi_2O_5$, and hence is a eutectic point, while all the others are transition points. The exact position of Q_5 is uncertain, and it has been assumed that it lies on the line H_2O-$KHSi_2O_5$. Hence the curves V + L + $KHSi_2O_5$ + SiO_2 (curve 2) and V + L + $KHSi_2O_5$ + $K_2Si_2O_5$ (curve 4*b*) will coincide stably with each other and with the melting point curve of $KHSi_2O_5$ (a condensed system). If the phases $KHSi_2O_5$, L, and SiO were to lie on a straight line, the curves V + L + $KHSi_2O_5$ + SiO_2 (curve 2) and L + $K_2Si_2O_5$ + $KHSi_2O_5$ + SiO_2 (the condensed system) would coincide stably; if the phases V, $KHSi_2O_5$, and SiO_2 were to lie on a straight line, the curves V + L + $KHSi_2O_5$ + SiO_2 (curve 2) and V + $K_2Si_2O_5$ + $KHSi_2O_5$ + SiO_2 (curve 9) would coincide metastably. Hence the curve V + L + $KHSi_2O_5$ + SiO_2 (curve 2) (and also V + L + $KHSi_2O_5$ + $K_2Si_2O_5$ (curve 4*b*), since the two coincide at the invariant point) must lie between the stable portion of curve L + $K_2Si_2O_5$ + $KHSi_2O_5$ + SiO_2, the P-T curve of the condensed system, and the metastable portion of the curve V + $K_2Si_2O_5$ + $KHSi_2O_5$ + SiO_2 (curve 9), the dissociation pressure curve. Similar reasoning shows that curve $K_2Si_2O_5$ + SiO_2 + L + V (curve 11) must lie between the metastable portions of the P-T curve of the condensed system and the dissociation-pressure curve.

We have seen that from a knowledge of the composition of the phases we are able to fix the sequence of the P-T curves around a quintuple point. Also, knowing that the P-T curves of condensed systems go from the invariant point to regions of higher pressure and, in almost all cases, higher temperature, and that dissociation pressure curves go from the invariant point to regions of lower temperature and pressure, we are able to fix the position of the P-T curves within fairly narrow limits. Let us now consider the slopes of these P-T curves in more detail, and pay especial attention to the change in slope as we move along a curve.

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When all the phases have a fixed composition, as is the case in a dissociation-pressure curve when only one of the components is volatile, or when the composition of a variable phase changes but little with pressure, as is the case in the equilibrium between several solids and liquid, the P-T curve of a condensed system, the slope of the P-T curve changes but slowly. But when we have a phase whose composition changes materially as we move along the P-T curve, the slope of the curve may become radically different. In the first two cases mentioned, the value of $\Delta\eta/\Delta v$ changes but little; in the third case it may change materially in magnitude, and may even change sign. Let us examine this case in detail. To prevent our equations from becoming too cumbersome, we will restrict our discussion to systems of three components; all the equations developed can readily be extended to any other case by putting in the requisite number of composition terms in the determinantal coefficients.

We have seen that the relation between the variations in pressure and temperature in any univariant equilibrium is given by Gibbs' Equation 129, which for a 3-component system reduces to

$$\frac{dp}{dt} = \frac{\begin{vmatrix} \eta' & m_1' & m_2' & m_3' \\ \eta'' & m_1'' & m_2'' & m_3'' \\ \eta''' & m_1''' & m_2''' & m_3''' \\ \eta^{IV} & m_1^{IV} & m_2^{IV} & m_3^{IV} \end{vmatrix}}{\begin{vmatrix} v' & m_1' & m_2' & m_3' \\ v'' & m_1'' & m_2'' & m_3'' \\ v''' & m_1''' & m_2''' & m_3''' \\ v^{IV} & m_1^{IV} & m_2^{IV} & m_3^{IV} \end{vmatrix}}$$

In this the composition of the phases is represented by the actual masses of the components m_1, m_2, m_3. By setting $m_1 + m_2 + m_3 = 1$; $\frac{m_2}{m_1 + m_2 + m_3} = m_2 = x$; $\frac{m_3}{m_1 + m_2 + m_3} = m_3 = y$, and substituting, adding the third and fourth columns to the second, we get

$$\frac{dp}{dt} = \frac{\begin{vmatrix} \eta' & 1 & x' & y' \\ \eta'' & 1 & x'' & y'' \\ \eta''' & 1 & x''' & y''' \\ \eta^{IV} & 1 & x^{IV} & y^{IV} \end{vmatrix}}{\begin{vmatrix} v' & 1 & x' & y' \\ v'' & 1 & x'' & y'' \\ v''' & 1 & x''' & y''' \\ v^{IV} & 1 & x^{IV} & y^{IV} \end{vmatrix}}$$

in which the composition of the phases is represented by the mol fractions x and y of 2 of the components. Expansion of this gives

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$$\frac{dp}{dt} = \frac{\eta' \begin{vmatrix} 1 & x'' & y'' \\ 1 & x''' & y''' \\ 1 & x^{IV} & y^{IV} \end{vmatrix} - \eta'' \begin{vmatrix} 1 & x' & y' \\ 1 & x''' & y''' \\ 1 & x^{IV} & y^{IV} \end{vmatrix} + \eta''' \begin{vmatrix} 1 & x' & y' \\ 1 & x'' & y'' \\ 1 & x^{IV} & y^{IV} \end{vmatrix} - \eta^{IV} \begin{vmatrix} 1 & x' & y' \\ 1 & x'' & y'' \\ 1 & x''' & y''' \end{vmatrix}}{v' \begin{vmatrix} 1 & x'' & y'' \\ 1 & x''' & y''' \\ 1 & x^{IV} & y^{IV} \end{vmatrix} - v'' \begin{vmatrix} 1 & x' & y' \\ 1 & x''' & y''' \\ 1 & x^{IV} & y^{IV} \end{vmatrix} + v''' \begin{vmatrix} 1 & x' & y' \\ 1 & x'' & y'' \\ 1 & x^{IV} & y^{IV} \end{vmatrix} - v^{IV} \begin{vmatrix} 1 & x' & y' \\ 1 & x'' & y'' \\ 1 & x''' & y''' \end{vmatrix}}$$

Now the coefficients of η', v', η'', v'', etc., represent the areas of the triangles $P''P'''P^{IV}$, $P'P''P'''$, $P'P''P^{IV}$ and $P'P''P'''$, respectively.[1] It is important to bear in mind the direction in which a given triangle is circumscribed, since, if the area of the triangle $P'P''P'''$ is positive, the area of the triangle $P''P'P'''$ is negative.

Since the above coefficients represent areas, we will denote determinant by the letter A, followed by subscripts indicating which triangle is meant, and the direction in which it is to be circumscribed is given by the order of the subscripts. Thus A_{123} represents the determinant

$$\begin{vmatrix} 1 & x' & y' \\ 1 & x'' & y'' \\ 1 & x''' & y''' \end{vmatrix}$$

the area of the triangle $P'P''P_1''$. Our equation becomes

$$\frac{dp}{dt} = \frac{A_{234}\eta' - A_{134}\eta'' + A_{124}\eta''' - A_{123}\eta^{IV}}{A_{234}v' - A_{134}v'' + A_{124}v''' - A_{123}v^{IV}}.$$

Now it is easy to show that

$$\begin{vmatrix} 1 & x'' & y'' \\ 1 & x''' & y''' \\ 1 & x^{IV} & y^{IV} \end{vmatrix} + \begin{vmatrix} 1 & x' & y' \\ 1 & x'' & y'' \\ 1 & x^{IV} & y^{IV} \end{vmatrix} = \begin{vmatrix} 1 & x' & y' \\ 1 & x''' & y''' \\ 1 & x^{IV} & y^{IV} \end{vmatrix} + \begin{vmatrix} 1 & x' & y' \\ 1 & x'' & y'' \\ 1 & x''' & y''' \end{vmatrix}$$

or, expressed in areas, that

$$A_{234} + A_{124} = A_{134} + A_{123}.$$

Hence we can eliminate any one of the above coefficients,[2] and cast our equation into the form

$$\frac{dp}{dt} = \frac{(\eta''' - \eta^{IV}) + \frac{A_{234}}{A_{123}}(\eta' - \eta''') - \frac{A_{134}}{A_{123}}(\eta'' - \eta''')}{(v''' - v^{IV}) + \frac{A_{234}}{A_{123}}(v' - v''') - \frac{A_{134}}{A_{123}}(v'' - v''')}.$$

We will now apply this equation to the ternary equilibrium $K_2SiO_3.0.5H_2O + K_2Si_2O_5 + L + V$ (curve 6*c*), the curve which proceeds from the quintuple point Q_2 to quintuple point Q_1 (Fig. 3). Calling $K_2SiO_3.0.5H_2O$, S′, and $K_2Si_2O_5$, S″, our equation becomes

[1] In a 2-component system, the determinantal coefficient represents the lengths of lines; in a 4-component system, volumes of solids; in an *n*-component system the volume of an *n*-dimensional solid.

[2] A similar elimination can of course be made in the general case.

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$$\frac{dp}{dt} = \frac{(\eta^l - \eta^v) + \frac{A_{2lv}}{A_{12l}}(\eta' - \eta^l) - \frac{A_{1lv}}{A_{12l}}(\eta'' - \eta^l)}{(v^l - v^v) + \frac{A_{2lv}}{A_{12l}}(v' - v^l) \quad \frac{A_{1lu}}{A_{12l}}(v'' - v^l)}.$$

At Q_2, the terms $(\eta^l - \eta^v)$ and $(v^l - v^v)$, both of which are negative and much larger than the other terms, preponderate; dp/dt is positive. As with increasing temperature the liquid traces the curve Q_2Q_1, the triangle A_{12l} becomes smaller, while the triangles A_{2lv} and A_{1lv} become larger. The values of the coefficients of $(\eta' - \eta^l)$ and $(\eta'' - \eta^l)$ in the numerator and $(v' - v^l)$ and $(v'' - v^l)$ in the denominator thus increase rapidly. Since the value of $(v^l - v^v)$ is comparatively large, this increase in the coefficients at first affects materially the value of the numerator only. As the liquid follows the curve Q_2Q_1 the value of the last two terms of the numerator soon becomes equal to the value of the first term. The numerator then becomes zero, dp/dt becomes zero, and the curve has a horizontal tangent. It will be observed that such a point of maximum pressure is found on many of the P-T curves representing univariant equilibrium between two solids, liquid and vapor in the system. It is most pronounced in the univariant equilibrium $KHSi_2O_5 + SiO_2 + L + V$.

On further increase in temperature the numerator becomes positive, the denominator remains negative, hence dp/dt is negative. This continues until, in the case we are considering, the phase K_2SiO_3 makes its appearance at the quintuple point Q_1. Let us consider the metastable continuation of the curve $K_2SiO_3.0.5H_2O + K_2Si_2O_5 + L + V$ (Curve 6*c*).

Beyond Q_1, on further increase in temperature the triangle A_{12l} approaches zero, the coefficients of $(v' - v^l)$ and $(v'' - v^l)$ in the denominator increase rapidly, reaching such a value that the sum of the last two terms in the denominator become numerically equal to the first, in spite of the large value of $(v^l - v^v)$. The denominator then becomes zero, dp/dt becomes infinite, and the P-T curve has a vertical tangent. Beyond this point dp/dt again becomes positive. An illustration of this case is found in the P-T curves of the monovariant systems $K_2Si_2O_5 + KHSi_2O_5$ $L + V$ (curve 4*b*) and $SiO_2 + KHSi_2O_5 + L + V$ (curve 2), which proceed from Q_5 to higher temperature and pressure.

On further increase in temperature the liquid will lie on the line $K_2SiO_3.0.5H_2O - K_2Si_2O_5$; the area A_{12l} now is zero, and our equation becomes

$$\frac{dp}{dt} = \frac{A_{2lv} \quad (\eta' - \eta^l) - A_{1lv} \quad (\eta'' - \eta^l)}{A_{2lv} \quad (v' - v^l) - A_{1lv} \quad (v'' - v^l)}.$$

In harmony with our previous considerations, we see that at this point the curve has the same slope as the common melting-point curve of $K_2SiO_3.0.5H_2O + K_2Si_2O_5$. This is an illustration of the case that the phases only casually have such a composition that a linear relation is possible;

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the curves are tangent. In the usual case which we are assuming throughout, dp/dt is positive.

We will now consider the application of our equation to a different type of equilibrium between two solids, liquid and vapor. Consider the equilibrium $K_2Si_2O_5.H_2O + K_2Si_2O_5 + L + V$ (curve $7b + 7c$). In the concentration diagram the course of this equilibrium is the curve Q_2Q_4, the boundary curve between the $K_2Si_2O_5$ and $K_2Si_2O_5.H_2O$ fields. Since the two solid phases and vapor lie on a straight line our equation is

$$\frac{dp}{dt} = \frac{A_{234} \quad (\eta' - \eta^v) - A_{134} \quad (\eta'' - \eta^v)}{A_{234} \quad (v' - v^v) - A_{134} \quad (v'' - v^v)},$$

the equation of the dissociation pressure curve of $K_2Si_2O_5.H_2O$. Hence, as we saw before, the P-T curves of the equilibrium $K_2Si_2O_5.H_2O + K_2Si_2O_5 + L + V$ coincide with the dissociation-pressure curve of $K_2Si_2O_5.H_2O$. The slope of this curve will remain positive as we go along the boundary curve $K_2Si_2O_5 - K_2Si_2O_5.H_2O$, and will not show anything special until the liquid phase falls on the line $V - K_2Si_2O_5$. Here the two triangles A_{234} and A_{134} become zero at the same time, and our equation becomes intermediate. This point corresponds to the termination of the curve at the quadruple point $K_2Si_2O_5 + K_2Si_2O_5.H_2O + L + V$ in the binary system H_2O–$K_2Si_2O_5$. When the liquid has crossed the line H_2O-$K_2Si_2O_5$ the areas of all the triangles change sign, hence dp/dt remains positive, and with decreasing temperature we retrace the same P-T curve to the quintuple point Q_4. This portion of the curve also corresponds to the equilibrium $KHSi_2O_5 + K_2Si_2O_5 + K_2Si_2O_5.H_2O + V$.

In the first equilibrium we considered, the univariant equilibrium $K_2SiO_3.0.5H_2O + K_2Si_2O_5 + L + V$, our assumption that the vapor phase is pure H_2O was practically without influence; the vapor phase might contain appreciable quantities of either K_2O or SiO_2 or both without appreciably affecting the course of the P-T curve. The only effect would be a slight diminution of the areas A_{1l_v} and A_{2l_v}, the coefficients of $(\eta'' - \eta^l)$ and $(v'' - v^l)$, and $(\eta' - \eta^l)$ and $(v' - v^l)$, respectively. In the second case, however, the assumption is of importance; only in the improbable case that the ratio of SiO_2/K_2O in the vapor is the same as in the solid, *i. e.*, 2/1, would it still be true that equilibrium $K_2Si_2O_5 + K_2Si_2O_5.H_2O + L + V$ coincides with the equilibria $K_2Si_2O_5 + K_2Si_2O_5.H_2O + K_2SiO_3.0.5H_2O + V$ and $K_2Si_2O_5 + K_2Si_2O_5H_2O + KHSiO_5 + V$, and with the dissociation-pressure curve of $K_2Si_2O_5.H_2O$. In case the vapor contained a small amount of K_2O, the curve $K_2Si_2O_5 + K_2Si_2O_5.H_2O + L + V$ would consist of 2 parts, one on one side of, the other on the other side of, the dissociation-pressure curve, and the two parts would join at the top in a smooth curve, whose point of maximum temperature would be found at the point where the entropy change in the reaction passes

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through zero, hence on the K_2O side of the line $K_2Si_2O_5$ - $K_2Si_2O_5.H_2O$. But unless the K_2O content of the vapor is large, which is improbable, the effect will be small; the area $K_2Si_2O_5$ - $K_2Si_2O_5.H_2O$ - V, instead of being zero, will be a very small quantity, which will have but a slight influence on the above relations; the curves would, instead of coinciding, lie very close to each other.

All the P-T curves so far discussed have had their end points inside the component triangle; all of them have gone from one quintuple point to another. Let us now consider one which goes from a quintuple point to a quadruple point in one of the limiting binary systems, *e. g.*, the curve $K_2SiO_3 + K_2SiO_3.0.5H_2O + L + V$ (curve 10*b*), which goes from quintuple point Q_1 to the quadruple point $K_2SiO_3 + K_2SiO_3.0.5H_2O + L + V$ in the binary system H_2O–K_2SiO_3. Since the phases V, $K_2SiO_3.0.5H_2O$, and K_2SiO_3 lie on a straight line, the area of the triangle V-$K_2SiO_3.0.5H_2O$-K_2SiO_3 is zero, and the equation on the P-T curve reduces to

$$\frac{dp}{dt} = \frac{A_{2vl} \quad (\eta' - \eta'') - A_{1vl} \quad (\eta_1' - \eta'')}{A_{2vl} \quad (v' - v'') - A_{1vl} \quad (v_1' - v'')}$$

in which the exponents (′) and (″) refer to the solid phases K_2SiO_3 and $K_2SiO_3.0.5H_2O$, respectively. This is evidently the dissociation-pressure curve of $K_2SiO_3.0.5H_2O$; in harmony with our previous conclusions, the slope of the curve $K_2SiO + K_2SiO_3.0.5H_2O + L + V$ (10*b*) is the same as that of the dissociation-pressure curve of $K_2SiO_3.0.5H_2O$ (10*a* + 10*b*). At the quintuple point it is evident that both numerator and denominator are negative, dp/dt therefore positive. Also, the denominator being much larger than the numerator, the numerical value of dp/dt is less than unity. As the liquid approaches the side of the component triangle along the boundary curve, both the triangles A_{2vl} and A_{1vl} diminish the size in about the same proportion, and the value of dp/dt will not change materially. When the liquid gets on the line H_2O-K_2SiO_3, both triangles become zero simultaneously, and the equation becomes indeterminate; the curve is at its end point at the quadruple point in the binary system.

It is evident that when the phases have the composition indicated above, no maximum is possible in the P-T curve of the univariant equilibrium. However, if the vapor phase, instead of being pure H_2O, contained a small amount of SiO_2, the curve would have a horizontal tangent before the phases L, $K_2SiO_3.0.5H_2O$, and K_2SiO_3 fell on a straight line, as can be readily seen from the equation of the curve.

In the preceding paper the theorem that along a boundary curve in a condensed system the temperature is a maximum at the point where the boundary curve crosses the line joining the composition of the two solid phases is derived. It is interesting to compare the condition for maximum temperature under the vapor pressure of the system. An example

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is the curve $K_2Si_2O_5 + KHSi_2O_5 + L + V$ (curve 4*b*), which goes from Q_4 to Q_5. The equation of this curve is

$$\frac{dp}{dt} = \frac{(\eta^l - \eta^v) + \frac{A_{1lv}}{A_{12l}}(\eta' - \eta^l) - \frac{A_{1lv}}{A_{12l}}(\eta'' - \eta^l)}{(v^l - v^v) + \frac{A_{2lv}}{A_{12l}}(v' - v^l) - \frac{A_{1lv}}{A_{12l}}(v'' - v^l)},$$

in which the exponents (′) and (″) refer to the phases $K_2Si_2O_5$ and $KHSi_2O_5$, respectively. The condition for a temperature maximum is that the denominator of this expression shall become zero; dp/dt become infinite. Since the volume difference between vapor and liquid is far greater than that between solid and liquid, the denominator will become zero only when the coefficients of the last two volume differences become very large, hence when the area of the triangle $K_2Si_2O_5$ - $KHSi_2O_5$ - L be comes very small. This point will be reached slightly before the liquid phase lies on the line $K_2Si_2O_5$ - $KHSi_2O_5$, hence the point of maximum temperature has been displaced slightly in the direction of the volatile component.

Summary.

In this paper the curves which represent the relation between the variations in pressure and temperature in monvariant systems, the P-T curves, are discussed on the basis of equations deduced by Gibbs. Theorems are developed showing under what conditions different P-T curves coincide, when the curves coincide throughout their course and when they are tangent, and whether they coincide in their stable or metastable portions. On the basis of the above theorems a method is developed for determining the order of successsion of the P-T curves which intersect at an invariant in a system of any number of components. This application is illustrated by applying it to the P-T curves proceeding from the quintuple points in the ternary system H_2O–K_2SiO_3–SiO_2. In addition, Gibbs' general equation for the slope of a P-T curve is discussed, and a method given for casting it into a form convenient for practical use. The application of this equation to the change in slope of a P-T curve with change in composition of a variable phase is illustrated by discussing various curves in the above-mentioned ternary system.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF OHIO STATE UNIVERSITY.]

A LEAD STANDARD CELL AND A DETERMINATION OF THE POTENTIAL OF THE LEAD ELECTRODE.

BY W. E. HENDERSON AND GEBHARD STEGEMAN.

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While engaged in a study of the transition temperature of some hydrated salts, a galvanic cell came under our observation which exhibited

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some interesting features, namely, its constancy of electromotive force and its reproducibility. An extended study was made of this cell, and the results appear in the following article.

The cell under consideration consisted in the following arrangement:

$$\text{Pb amalgam} — PbSO_4 — Na_2SO_4 10H_2O — Hg_2SO_4 — Hg$$

A study of lead amalgams has been made by Puschin,[1] and he has found that all amalgams having a percentage of lead between 1.8% and 66% exhibited the same electromotive force. Fay and North[2] state that an amalgam having a percentage of lead between the limits of about 2% and 55% is a two-phase system, consisting of a granular phase of constant composition (Pb_2Hg), and a liquid phase which also has a definite composition when equilibrium is reached. In the present investigation it has been found that amalgams having a percentage of lead between 2.5% and 6% possess a constant and reproducible electromotive force. Amalgams of higher concentration have not yet been studied by us. Such an amalgam should therefore serve well as one of the electrodes in a standard cell, and the results of this investigation appear to support this conclusion.

Preparation of Materials.

(*a*) **Lead Amalgams.**—The lead amalgams used were prepared by the electrolysis of a 10% solution of pure lead nitrate, using a mercury cathode and a platinum anode. A current of approximately 20 milliamperes was allowed to pass until the amalgam contained the desired percentage of lead, usually between 2.5% and 6% of lead.

(*b*) **Lead Sulfate.**—A dilute solution of sulfuric acid was slowly added to a dilute solution of lead nitrate and the precipitated sulfate repeatedly washed with distilled water. It was kept under water until ready to be used.

(*c*) **Sodium Sulfate.**—Three recrystallizations from distilled water were made to purify this salt. The crystals were kept in a moist condition to avoid efflorescence.

(*d*) **Mercurous Sulfate.**—The method described by Hulett[3] consisting in electrolyzing a solution of sulfuric acid (sp. gr. 1.15) with a mercury anode, was carefully followed. The gray product of this electrolysis was preserved in a dark-colored bottle under the acid used in its preparation.

(*e*) **Mercury.**—Ordinary mercury was stirred for two days in contact with dilute nitric acid and was then twice distilled under reduced pressure.

Preparation of the Cell.

The H type of cell was found to be very convenient and was made by joining two "culture tubes" together at a distance of about five cm. from

[1] *Z. anorg. allgem. Chem.*, **36**, 201 (1903).

[2] *Am. Chem. J.*, **25**, 216 (1901).

[3] *Phys. Rev.*, **22**, 334 (1906).

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the closed end. The amalgam was placed in one leg of the cell by means of a small bore pipet and mercury was introduced into the other leg in a similar manner. A paste composed of an intimate mixture of lead sulfate and sodium sulfate moistened with a solution saturated with both of these salts, was placed over the amalgam. Upon the mercury was placed a paste composed of an intimate mixture of lead sulfate, sodium sulfate and mercurous sulfate moistened by the previously mentioned solution. The sodium sulfate crystals comprised the largest part of the mixture. Both the lead sulfate and mercurous sulfate were washed free from acid (in a Gooch crucible) before being used in the cell in the manner employed by Hulett,[1] except that no alcohol was used. The washing material consisted of an aqueous solution saturated with both lead sulfate and sodium sulfate. An intimate mixture of lead sulfate and sodium sulfate was then used to fill up the cell to the cross arm, after which enough of the solution of lead sulfate and sodium sulfate was introduced to cover the crystals and fill the cross arm of the cell. Platinum wires sealed into small glass tubes extended down into both the amalgam and the mercury and served as a means of contact. Small cork stoppers, perforated to allow the passage of the wires, served to close the cell when it was placed in the thermostat. A little melted paraffin was then poured upon the stoppers, making them water-tight. The cells were kept at the desired temperature by placing them in a thermostat regulated to 0.01°.

A potentiometer reading directly to 0.00001 volt, in connection with a sensitive galvanometer, was used in making all measurements. A lead accumulator was employed as the source of current for the potentiometer and two certified Weston standard cells served as reference.

Two cells were prepared on December 12, 1916, and measurements of the voltages exhibited were made at frequent intervals to determine the constancy. The following table shows the readings obtained:

TABLE I.

Cell I. Amalgam 2.6% Pb.	Cell II. Amalgam 3.5% Pb.	Time of reading.	Temp.
0.96470	0.96453	Dec. 12, 1916	25°
0.96465	0.96470	Jan. 18, 1917	25°
0.96465	0.96465	Feb. 2, 1917	25°
0.96463	0.96464	March 2, 1917	25°
0.96463	0.96464	April 6, 1917	25°
0.96342	0.96343	April 15, 1917	18°
0.96342	0.96343	April 18, 1917	18°
0.96550	0.96552	April 19, 1917	30°
0.96550	0.96552	April 21, 1917	30°

To determine the reproducibility of this type of cell three new cells were prepared on February 12, 1917, and the voltages compared with those previously made.

[1] Hulett, THIS JOURNAL, 38, 23 (1916); cf. also *Phys. Rev.*, 22, 234 (1906).

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TABLE II.

Cell III.	Cell IV.	Cell V.	Time.	Temp.
0.96465	0.96461	0.96464	Feb. 12, 1917	25°
0.96465	0.96462	0.96463	Feb. 18, 1917	25°
0.96465	0.96462	0.96463	Mar. 12, 1917	25°
0.96464	0.96461	0.96462	Apr. 18, 1917	25°

This table shows that this cell is reproducible to within 3 hundredths of a millivolt, though a gradual decrease in voltage is noticeable over an extended range of time, a condition sometimes found in Weston and Clark cells. The electromotive force of this cell at any desired temperature may be found by means of the following equation, which has been verified by the values obtained at 18° and 30°, and shown in Table I:

$$E_t = 0.96463 + 0.000174\,(t - 25) + 0.00000038\,(t - 25)^2 \quad (1)$$

Calculation of the Heat Reaction.

In order to compare the heat of the reaction occurring in the cell, *viz.*,

$$0.5\ Pb_2Hg + Hg_2SO_4 \longrightarrow PbSO_4 + 2.5\ Hg,$$

with the available thermochemical data obtained at 18° by Thomsen, it is necessary to substitute the measured values of the cell in the Gibbs-Helmholtz equation:

$$Q = nF\left(E - T\frac{dE}{dT}\right)0.2387$$

At 18° the e. m. f. of the cell has been found to be 0.96343 volt, while the value of dE/dT, found by differentiating Equation 1, is +0.000169. The Gibbs-Helmholtz equation then assumes the form

$$Q = 2F\,(0.96343 - 291 \times 0.000169)\,0.2387 = 42{,}139 \text{ cals.}$$

Thomsen gives the heat of formation of lead sulfate as 216,200 cals. at 18°, while that of mercurous sulfate is given as 175,000 cals. The difference, 41,200 cals., then represents the free energy of the reaction

$$Pb + Hg_2SO_4 \longrightarrow PbSO_4 + 2Hg.$$

According to Luther,[1] an evolution of energy amounting to +585 cals. takes place when one gram-atom of lead is removed from the heterogeneous amalgam of which the solid phase is the compound Pb_2Hg. The true heat of reaction occurring in the cell, based upon thermochemical measurements, is therefore 41,200 + 585 or 41,785 cals.

Determination of the Potential of the Lead Electrode.

The constancy of the voltage of a lead amalgam such as was employed in the preparation of the cell described suggested that such an amalgam might be used in the determination of the potential of the lead electrode provided the difference in voltage between such an amalgam and a solid lead electrode were accurately known. A number of cells were accord-

[1] *Z. Elektrochem.*, 17, 293 (1911).

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ingly prepared identical in every respect with those before described except that a solid lead electrode, made by precipitating lead electrolytically upon a heavy platinum wire from a 10% solution of lead nitrate, was substituted for the usual amalgam. Such electrodes were found to give a very constant voltage for at least two days, after which the voltage appeared to drop gradually. The fluctuation in voltage described by Getman[1] when lead precipitated upon platinum is placed in a solution of lead chloride was not apparent in these cells wherein the lead salt was the sulfate. The following table gives the voltage of four cells prepared in this manner:

Cell I.	Cell II.	Cell III.	Cell IV.	Temp.
0.96988	0.96965	0.96969	0.96972	25°

The difference between the mean value, 0.96973 and 0.96463, amounting to 0.0051 volt, is the difference in voltage existing between solid lead and the amalgam used in the cells.

The difference in potential existing between a 2 or 3% amalgam and a saturated solution of lead chloride which had been purified by two recrystallizations, was then measured against a battery of three electrodes constructed of the series 0.1 N KCl-Hg_2Cl_2-Hg. The calomel used in these electrodes was prepared by the electrolysis of a normal solution of hydrochloric acid with a mercury anode. The calomel was washed free from acid with a 0.1 N KCl solution before being used in the cell. The following values were obtained:

Amalgam I.	Amalgam II.	Amalgam III.	Amalgam IV.	Temp.
0.5138	0.5137	0.5135	0.5136	25°

There was no appreciable fluctuation in voltage during a two-day period so the mean of the values here given, 0.51367, is taken as the difference of potential existing between the amalgams used and an aqueous solution saturated with lead chloride. All of the amalgams were of different composition, ranging between 2% and 4% of lead. The resistance of the chain whose voltage was measured was so great that differences of 0.0001 volt were the smallest that could be accurately determined. Adding the value 0.0051 which is the difference between the amalgams used and a solid lead electrode we obtain 0.5187 volt as the potential of the chain

$$Pb - PbCl_2 \text{ sat.} - 0.1\ N\ KCl - Hg_2Cl_2 - Hg.$$

The Solubility of Lead Chloride and the Degree of Dissociation at This Dilution.

The solubility of lead chloride in water at 25° is given by D. M. Lichty[2] as 0.0388 mol per liter. The activity of the lead ion is given by Noyes and Toabe[3] at this dilution as 0.562 but is based, according to their state-

[1] THIS JOURNAL, 38, 792 (1916).

[2] *Ibid.*, 25, 469 (1903).

[3] *Ibid.*, 39, 1537 (1917).

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ment, upon conductivity data and may therefore be subject to some error.

Since this work was done an article has appeared by Lewis and Brighton[1] in which they express the hope that in the near future they will be able to calculate the activity of the lead ion in a solution saturated with lead chloride. On the assumption that the activity of the lead ion in a saturated solution of lead chloride is 0.562% of the total concentration, the potential of the lead electrode is readily calculated by the equation

$$E = E^\circ - \frac{RT}{2F} \ln C$$

in which

E = 0.5187
E° = normal electrode potential
C = concentration in mols of the ion in question.

The equation then assumes the form

$$0.5187 = E^\circ - \frac{RT}{2F} \ln (0.0388 \times 0.562) \text{ or } E^\circ = 0.4696.$$

This is the value of the normal electrode of lead against the 0.1 *N* calomel electrode at 25°.

Summary.

A lead standard cell has been prepared which has been found to possess a constant voltage which is reproducible to within a few hundredths of a millivolt. It has been found that the voltage shows a gradual decrease over an extended range of time, a property frequently found in other cells.

A determination of the potential of the lead electrode against the tenth normal calomel electrode has been made and found to be 0.4696 at 25°. This value may be subject to a change when the activity of the lead ion in the solution in question becomes more accurately known.

COLUMBUS, OHIO.

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY.]

THE TRANSITION TEMPERATURES OF STRONTIUM CHLORIDE AND STRONTIUM BROMIDE AS FIXED POINTS IN THERMOMETRY.

BY THEODORE W. RICHARDS AND VICTOR YNGVE.

Received October 29, 1917.

Introduction.

Some years ago one of us[2] pointed out that the transition temperatures of hydrated salts, since they are invariant points, serve excellently as

[1] THIS JOURNAL, 39, 1906 (1917).
[2] T. W. Richards, *Am. J. Sci.*, [4] 6, 201 (1898).

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fixed points in thermometry. The accuracy of this method of fixing temperatures has since been confirmed and its usefulness extended. The transition temperatures which have been the subject of careful investigation at Harvard are given below.

Transition system.	Transition temperature.
$Na_2SO_4.10H_2O$ to Na_2SO_4 + solution[1]	32.383°
$NaBr.2H_2O$ to NaBr + solution[2]	50.674°
$MnCl_2.4H_2O$ to $MnCl_2.2H_2O$ + solution[3]	58.089°
$Na_2CrO_4.10H_2O$ to $Na_2CrO_4.6H_2O$ + solution[4]	19.525°
$Na_2CrO_4.10H_2O$ to $Na_2CrO_4.4H_2O$ + solution[4]	19.987°
$Na_2CO_3.10H_2O$ to $Na_2CO_3.7H_2O$ + solution[5]	32.017°

The present investigation adds to these the transition temperature (61.341°) of strontium chloride hexahydrate into the dihydrate, as well as a similar but merely preliminary result (88.62°) concerning strontium bromide.

In a preliminary manner the transition of strontium chloride hexahydrate had already been tested.[6] The transition temperature, about 61°, was found to be easily maintained, and appeared to possess the required degree of constancy. Tammann[7] had studied the effect of pressure upon the temperature of transition of strontium chloride hexahydrate; but an exact determination of this temperature seemed to be lacking. No reference has been found to a direct determination of the transition temperature of strontium bromide. Lescoeur[8] found that the dissociation tension of the hexahydrate of strontium bromide was less than that of a saturated solution of the salt at 20° and 40°, but that at 100° they were approximately equal. He concluded that a transition to a lower hydrate occurred at about this temperature—but strictly speaking no evidence was afforded as to where, between 40° and 100°, the transition actually occurred.

[1] Richards and Churchill, *Proc. Am. Acad.*, **34**, 277 (1899); Richards and Wells, *Ibid.*, **38**, 431 (1903); Dickinson and Mueller, THIS JOURNAL, **29**, 1381 (1907), give 32.384° as the temperature of the transition.

[2] Richards and Wells, *Proc. Am. Acad.*, **41**, 435 (1906).

[3] Richards and Wrede, *Ibid.*, **43**, 343 (1907).

[4] Richards and Kelley, *Ibid.*, **47**, 171 (1911).

[5] Richards and Fiske, THIS JOURNAL, **36**, 485 (1914).

[6] Richards and Churchill, *Proc. Am. Acad.*, **34**, 277 (1899). Jeannel proposed to use the transition temperature of sodium acetate trihydrate (about 58°) as a thermometric fixed point "for constructing or calibrating thermometers" (*Compt. rend.*, **62**, 834 (1866)). This fact was not known to us until 1914 (THIS JOURNAL, **36**, 486 (1914)) and seems not to have made any impression on others nor to have been ever put to use.

[7] Tammann, "Krystalliseren und Schmelzen," 1903, p. 251. This notice refers to the earlier work of Kremers, Mulder, and v. Sahmen, who found the values 60°, 66°, and 62.2°, respectively.

[8] Lescoeur, *Ann. chim. phys.*, [6] **19**, 554 (1890).

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The Hydrates of Strontium Chloride.

Andreae[1] concluded from vapor-pressure measurements on the hydrates of strontium chloride that the hexahydrate passes into the dihydrate, a conclusion which we have confirmed by analysis of the transition product. In order to prevent the solidification of the adhering liquid phase on cooling, or during filtration, this latter process was conducted in closed vessels suitably arranged so that the whole process could be conducted in a thermostat at about 62° in a current of air previously moistened so as to be in hygroscopic equilibrium with the mixture. When no more liquid drained from the solid hydrate, it was removed, analyzed, and found to contain 2.29 H_2O. The slight excess of 0.29 H_2O was doubtless due to incomplete draining.

Purification of Strontium Chloride.

Calcium and barium are the two impurities which are the most difficult to eliminate from salts of strontium, because of the chemical similarity of these elements and the frequent tendency of their salts to form isomorphous crystals. The effect of recrystallizing strontium chloride as a means of eliminating these impurities was tested as follows: About 1% of each of the chlorides of barium and calcium was added to 20 g. of the strontium salt, the mixture recrystallized as hexahydrate, and the resulting crystals centrifuged and washed twice in the centrifuge. After three such recrystallizations practically no trace of barium could be found in the solid phase, while distinct evidences of the presence of calcium were found. Evidently barium is very rapidly eliminated from the hexahydrate, but calcium is eliminated but slowly, as would be expected from the usual forms in which the several salts occur at room temperature. On the other hand, we found that calcium can be eliminated by recrystallizing the dihydrate above the transition temperature, a process which, although it eliminates calcium, concentrates barium into the crystals instead of eliminating it from them. These two contrasting phenomena open the way for the complete purification of the salt, merely by crystallizing first above and then below 61.34°.[2] Great care must be taken to maintain the proper temperature in each case and to inoculate the solution with the proper hydrate. This is particularly necessary in the case of the hexahydrate, for the dihydrate may easily be obtained at temperatures below 61° unless due precaution is taken.

This double process, which was used in preparing one sample of chloride, is perhaps the best method yet found for freeing strontium from its

[1] *Z. physik. Chem.*, 7, 248 (1891).

[2] In some cases the order of crystallization might profitably be reversed, since crystallization at lower temperatures attacks the vessels less seriously, and the smaller quantities of the final processes are easier to handle in platinum or quartz than the large initial quantities.

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analogs, because it does not involve any change of the anion, with the consequent danger of the introduction of other impurities. Moreover, purification is more speedily and easily attained than with any other process.

The principle involved in this method may well be of use in many other cases, for it rarely happens that a given impurity is isomorphous with two differently hydrated forms of a given salt. Hence, usually, crystallizing as one hydrate will eliminate one set of impurities, and as another hydrate will eliminate another set. Often, doubtless, all the impurities will thus be eliminated either first or last, as in the case of strontium chloride.

The nitrate of strontium also may be used as a means of purification, at least from calcium, if similar precautions are taken. From the tetrahydrated nitrate the elimination of both barium and calcium by crystallization is slow and unsatisfactory, but from the anhydrous nitrate calcium may be eliminated in a satisfactory manner, the barium being concentrated in the crystals. Hence strontium may be purified by recrystallizing first as the anhydrous nitrate until calcium is eliminated, and then as hexahydrated chloride until barium is eliminated; but on the whole this process is not so satisfactory as that in which the chloride alone is used in two different stages of hydration.

This more complicated process was used first in our work, the better one having not been perfected. The solution of over a kg. of commercially pure nitrate was heated to boiling, acidified, and hydrogen peroxide added to oxidize iron which might be present. Strontium hydroxide, from oxide prepared by igniting the pure nitrate, was now added until the solution was alkaline, the solution was filtered through a washed filter paper and the nitrate was recrystallized hot four times in porcelain. After each crystallization it was drained centrifugally and washed twice with pure warm water, for if cold water is used in washing the tetrahydrate is formed and calcium retained. The resulting salt will be referred to as Sample E. The extreme mother liquor from the last sample was concentrated and tested spectroscopically for calcium, but no evidence of calcium was found. Suitable trials showed that 0.005 mg. of calcium could be detected under similar conditions. Hence the crystallized samples of nitrate were probably very free from this impurity, since it tends toward the solution.

The nitrate was now converted into the carbonate by treatment with the distillate from a mixture of pure ammonium carbonate and hydroxide in water. The strontium carbonate was separated from the supernatant ammonium nitrate by filtration through a hardened, washed filter paper in a large Gooch crucible, and was washed with several liters of water, and dissolved in pure hydrochloric acid.

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The strontium chloride thus prepared after seven crystallizations (two in porcelain and five in quartz) yielded Sample *e*. The transition temperature of this sample did not differ from that of the previous crop of crystals. Sample *f* was obtained by recrystallizing *e* in quartz. Sample D was obtained by recrystallizing six times in porcelain the mother liquors from the preparation of Sample *e*. Sample E was made by further recrystallizing D in porcelain; of these, Sample *f* was, of course, the purest.

The very convenient first-mentioned method was now used in the preparation of a new series of samples of strontium chloride.

The purest strontium chloride of commerce was recrystallized twice, in porcelain, as the dihydrate above 62°. The extreme mother liquor from the last crystallization showed, when concentrated, no traces of calcium when examined spectroscopically. The crystallized chloride was then recrystallized twice, in porcelain, as the hexahydrate. This yielded Sample L. Sample M was obtained by recrystallizing L in porcelain, and the identity of its transition temperature with that of L showed that the barium had been eliminated even from L. As will be seen, both temperatures agreed essentially with those of the purest salt *f* prepared from the nitrate. Thus strontium chloride is really very easy to purify.

The Transition Temperature of Strontium Chloride, $SrCl_2.6H_2O$ to $SrCl_2.2H_2O$.

The apparatus used in the determination of the transition temperatures was essentially identical with that used by Richards and Wrede.[1] A tall beaker 37 cm. in height and 14 cm. in diameter was used as the external bath. A large tube, closed at one end, 35 cm. long and 3 cm. in diameter, was supported within the bath to serve as an air jacket. Inside this tube was placed a smaller one, of a practically insoluble glass, 2 cm. in diameter and 30 cm. long. This inner tube was fitted with a stirrer—a stout platinum wire bent into a ring and sealed to a glass rod.

In addition to the stirrer and the standard thermometer, the inner tube also contained an auxiliary thermometer for determining the temperature of the emergent thread, since the larger tube was not wholly below the water in the bath. There was usually a small correction on this account. In order to remove all doubt as to the value of this correction, in some of the determinations a small heating coil of resistance wire was placed in the upper part of the tube and enough electrical energy was passed through the wire to heat the air in the tube to the temperature of the bulb of the thermometer. The correction determined in this manner was 0.003 of a degree, while that computed from the reading of the auxiliary thermometer was 0.004 of a degree. The first value was used in correcting all the readings.

The thermometer used was Baudin thermometer 15275, standardized

[1] *Proc. Am. Acad. Sci.*, **43**, 344 (1907).

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with great care at the Bureau des Poids et Mesures, and previously described.[1] It was read by means of an accurate cathetometer from both sides in order to eliminate errors which might be due to irregularities in the glass or a possible deviation of the thermometer from a truly vertical position. The ice points were taken immediately after reading the transition temperatures, and all the precautions mentioned by Guillaume[2] were observed.

The crystals of strontium chloride hexahydrate were placed in the inner 2 cm. tube, and this was warmed for a few minutes in a beaker of water kept a few degrees above the temperature of transition. When the mixture assumed a plastic condition the tube was dried and put in place, and the temperature readings were taken. The ice points, even when taken with all known precautions, are the most uncertain part of this work.

SAMPLE L, DETERMINATION I, MARCH 15, 1915.

Thermometer 15275:		
Barometer reduced	749.0 mm.	749.0 mm.
24 mm. inverting mixt	3.1	...
58 mm. water	...	4.3
	752.1 mm.	753.3 mm.
Reading in salt	61.464° In ice	+0.052
Correction calibration	—0.013	0.000
Correction exterior press	+0.001	+0.001
Correction interior press	+0.044	+0.013
Corrected reading in ice	—0.066	+0.066°
Correction for fundamental interval	—0.001	
Correction to hydrogen scale	—0.088	
Final corrected result	61.341°	

Eleven such final corrected results, from six different samples of salt, were thus obtained, and are given below. The "probable errors" computed according to the theory of least squares are appended.

TABLE II.

Transition Temperatures of Strontium Chloride.

Date 1915.	Sample.	Temperature.	Date 1915.	Sample.	Temperature.
Feb. 26	*e*	61.331°	Mar. 23	E	61.342°
Mar. 1	*e*	61.334	Mar. 15	L	61.341
Mar. 2	*f*	61.337	Mar. 16	L	61.340
Mar. 8	D	61.333	Mar. 19	M	61.344
Mar. 9	D	61.333	Mar. 24	M	61.338
Mar. 17	D	61.335			
			Total mean,		61.337° ± 0.001°
			Mean of last five,		61.341° ± 0.0007°

[1] Richards and Wells, *Proc. Am. Acad. Sci.*, **38**, 43 (1902).

[2] Guillaume, "Traité pratique de la Thermometrie de Precision," 1889.

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The determinations are seemingly divided into two groups, the first six and the last five. Of these groups, as usual, the later seems to be the more trustworthy. The technique was then more familiar and the ice points more convincing than at first. Moreover, the salt used in the last five trials was probably purer than the earlier samples, except Sample *f*, which gave a reading almost as high as the later ones.

Accordingly, 61.341°, or, roughly, 61.34°, is the most probable value of the temperature transition of the hexahydrate of strontium chloride into the dihydrate under atmospheric pressure, in terms of the international hydrogen scale.

The Hydrates and Transition Temperature of Strontium Bromide.

The hexahydrate of strontium bromide is well known, but the composition of the next lower hydrate does not seem to have been determined. Experiments conducted in the same manner as those described above with strontium chloride gave fairly convincing but not absolutely final evidence that this is a dihydrate, analogous to the corresponding chloride. The bromide used was prepared according to a method used in an early determination of the atomic weight of strontium.[1] Its acid solution had remained for some time in the glass vessel, but it was recrystallized five times afterwards, and the last two crops of crystals gave the same transition temperature. This determination was made in the same apparatus which served for the foregoing work with the chloride, and as a result the temperature of the transition was found to be 88.62°. Although not final, this value seems to be more trustworthy than most of those heretofore published, concerning data of this kind, except those quoted on the first page. We are glad to express our indebtedness to the Carnegie Institution of Washington for some of the apparatus and material used in this research.

Summary.

Two methods for preparing pure strontium chloride are described.

The existence of strontium chloride dihydrate has been confirmed.

The temperature of the transition of the hexahydrate of strontium chloride into the dihydrate has been found to be approximately 61.341° on the international hydrogen scale.

Evidence has been found which points to the existence of strontium bromide dihydrate.

The temperature of the transition of strontium bromide hexahydrate into the lower hydrate has been found to be approximately 88.62° on the international hydrogen scale.

CAMBRIDGE, MASS.

[1] Richards, *Proc. Am. Acad. Sci.*, 30, 369 (1894).

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TEMPERATURE DETERMINATIONS BY EUTECTIC ALLOYS.

By Charles P. Steinmetz.

Received October 23, 1917.

The melting points of pure metals give definite and sharply defined temperature points, and as such are of use in locating standard temperatures, and in the calibration of temperature measuring devices. As the melting points of eutectic alloys also occur at definite and sharply defined temperature points, it appears that eutectic alloys may be useful in temperature standardizations and measurements, and, due to their particular characteristics, may even be more convenient and therefore preferable to pure metals, especially in industrial applications.

As there are many more eutectic alloys than pure metals, and the former cover a wider range of temperatures, the use of eutectic alloys would give a far closer temperature scale, permitting their use not only for standardization of temperature measuring devices, but to some extent even directly for temperature measurements.[1] The foremost advantage expected from eutectic alloys was the far greater independence of their melting point from the purity of the material. With a pure metal, the melting point is very greatly affected, almost always lowered, by even small traces of impurities[2] and a very high degree of purity thus is essential. This greatly limits the availability, requires a high degree of care and precaution in the use, in guarding the material against contamination, and often limits its repeated use, thus making the use of pure metals for temperature calibration rather more a laboratory matter.

A eutectic alloy is that composition of constituents, which has the lowest melting point. Hence it is to be expected that any impurity, even when fairly considerable, should not affect the melting point. Any impurity, such as an excess of one or more constituents, would, in cooling, crystallize out when the freezing point is approached and the alloy thus thickens before solidifying, but the final freezing point remains that of the eutectic alloy. Inversely, in heating, only the eutectic would melt at the critical temperature, any impurity remain solid, and the alloy becomes very fluid only some degrees above the melting point, although the temperature of the melting point itself should not be affected.

Some experiments were then made, in the usual manner by the deter-

[1] The above investigation was suggested by the industrial problem of measuring maximum temperatures existing locally at the rim of steel discs revolving at such extremely high peripheral speeds that centrifugal forces precluded the attachment of any temperature measuring device to the rim of the rotor (steam turbine alternator) at which the temperature was desired. By drilling a series of small holes into the rim of the rotor at those places, where the temperature is desired, and filling the same with various eutectic alloys, the local temperature is located between the melting points of the two successive eutectics, of which the one is melted and thrown out centrifugally, while the next higher one remained.

[2] Thus 1% of zinc lowers the melting point of tin by about 4°.

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mination of the cooling curves, to see whether and how far the melting point of eutectic alloys is affected by impurities. The alloy was melted and allowed to cool, while stirring with the thermometer, and every 15 (or 30) seconds the temperature recorded, and temperature plotted against time. The thermometer was checked against a standard calibrated by the Reichsanstalt. Alloys with melting points below 200° were used, partly as they permit melting in test tubes and the use of mercury thermometer for temperature measurements, and also because a series of low melting eutectic alloys was desired by the industrial problem which led to the investigation. A very great tendency to undercooling was found with many alloys, and had to be counteracted by stirring.

The deviation of the alloy from a eutectic may be due to

(1) A deficiency of one or more of its constituents.

(2) An excess of one or more of its constituents.

(3) The presence of some metal which is not a constituent of the eutectic alloy.

All three cases were investigated and are shown by the cooling curves in Figs. 1, 2 and 3.

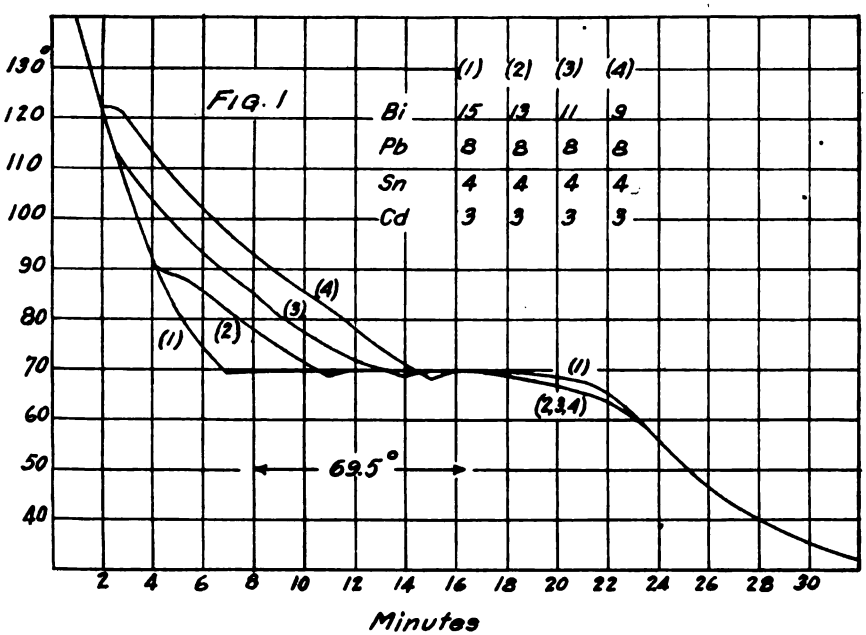

Fig. 1 shows as (1) the eutectic alloy, usually called Wood's Metal,

$$\text{Bi} \div \text{Pb} \div \text{Sn} \div \text{Cd} = 15 \div 8 \div 4 \div 3, \qquad (1)$$

giving a very long and sharply defined horizontal range at the temperature of 69.5°.

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(2), (3) and (4) of Fig. 1 differ from (1) by successively greater deficiency of bismuth, up to 20% of the total alloy.

$$\text{Bi} \div \text{Pb} \div \text{Sn} \div \text{Cd} = 13 \div 8 \div 4 \div 3 \qquad (2)$$
$$11 \div 8 \div 4 \div 3 \qquad (3)$$
$$9 \div 8 \div 4 \div 3 \qquad (4)$$

As seen, the horizontal range successively shortens, and is preceded by a temperature range, during which the alloy gradually thickens; but the final freezing point, 69.5°, is not appreciably changed, though less marked.

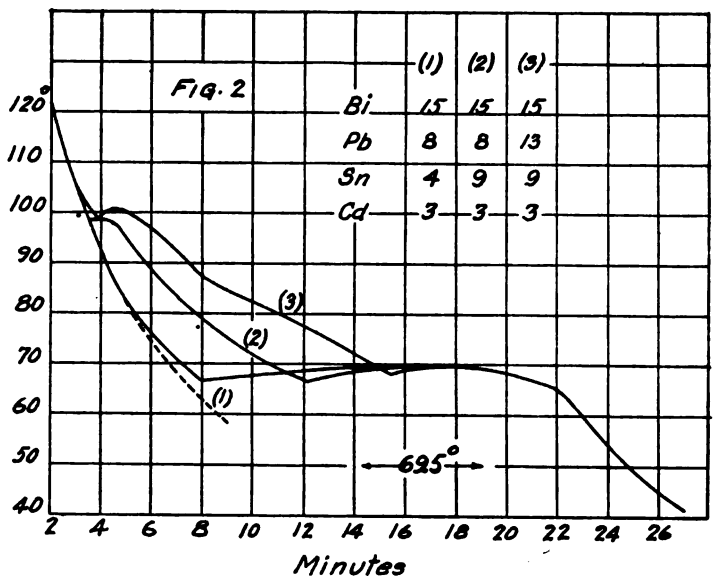

Fig. 2 shows as (1) the same eutectic alloy as (1) in Fig. 1, except that, due to insufficient stirring, considerable undercooling has taken place, and in freezing the temperature only gradually rises to the normal melting point, 69.5°.

(2) gives the same alloy with the addition of five parts (16.7%) of tin, and (3) the same alloy with the addition of five parts (16.7%) tin and five parts (16.7%) lead. That is,

$$\text{Bi} \div \text{Pb} \div \text{Sn} \div \text{Cd} = 15 \div 8 \div 4 \div 3 \qquad (1)$$
$$= 15 \div 8 \div 9 \div 3 \qquad (2)$$
$$= 15 \div 13 \div 9 \div 3 \qquad (3)$$

The characteristics are the same as in Fig. 1, a shortening of the constant temperature range during freezing, and an increasing range of gradual thickening, at gradually falling temperature, preceding the final freezing. However, the temperature of the final freezing point is not appreciably changed from 69.5°.

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(1) in Fig. 2 was a different sample of Wood's metal from that in Fig. 1, and apparently less pure as eutectic, showing a slight deviation from the exponential cooling curve (shown dotted) when approaching the freezing point.

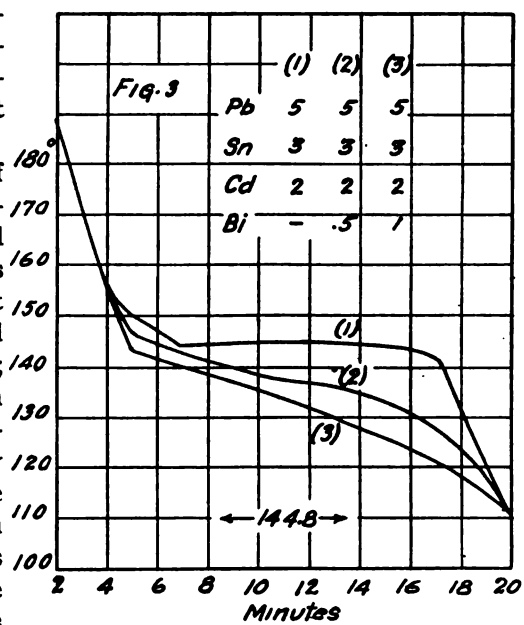
Fig. 3 shows as (1) the alloy

$$Pb \div Sn \div Cd = 5 \div 3 \div 2 \qquad (1)$$

with a sharply defined freezing point at 144.8° and as (2) and (3) two alloys produced by the addition of 5% and 10% bismuth, respectively.

$$Pb \div Sn \div Cd \div Bi = 5 \div 3 \div 2 \div 0.5 \qquad (2)$$
$$= 5 \div 3 \div 2 \div 1 \qquad (3)$$

Here, by the addition of a considerable quantity of a metal which does not belong in the eutectic alloy, the sharply defined freezing point disappears, the freezing temperature is lowered, and freezing occurs by a gradual thickening of the alloy throughout a temperature range.



Therefore in the use of eutectic alloys for temperature determinations, material impurities caused by metals which are not a constituent of the alloy, may be harmful and are to be guarded against; but a considerable deviation of the proportions of the normal constituents of the alloy appears harmless. Even the harmful effect of a foreign metal impurity probably is limited to the cases where the addition of such metal forms a eutectic alloy of lower melting point. For instance, the addition of zinc to the alloy (1) in Figs. 1 and 2 apparently has no effect in lowering the melting point, but merely causes a thickening of the alloy when approaching the freezing point.

When looking up the literature for eutectic alloys of low melting point, records of a large number were found, but most of them proved not to be eutectics, and the given melting points were frequently erroneous, due to disregarding the undercooling of the alloy.

The following twelve alloys were found in the range below 200°, which

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are eutectics or sufficiently near to eutectics in their composition, to permit their use, and their melting points determined by observing the freezing curves, while stirring with the thermometer. A number of observations were made with each alloy, with slightly changed composition, and by interpolation the composition of the true eutectic estimated and checked by its freezing curve.

However, neither time nor facilities were available to go very far in the investigation, and the values given in the following table thus are only approximately those of the eutectic. It would be of interest to determine the exact composition of the eutectic. This could most conveniently be done by studying the shape of the cooling curve. In the eutectic, the curve of decreasing temperature of the melted alloy follows an approximate exponential down to the constant freezing temperature, as in (1) of Fig. 1. If, however, the composition is not exactly eutectic, the cooling curve deviates from the exponential when approaching the freezing point, and the temperature decreases more slowly, while the non-eutectic part freezes out, as specially markedly seen in (1), Fig. 3 for instance.

LOW MELTING EUTECTIC ALLOYS.

(Approximate.)

Melting point.	Composition.						Remarks.	Temp. of undercooling.
	Bi.	Cd.	Pb.	Sn.	Tl	Zn.		
69.5[1]	15	3	8	4	..	..	slightly ductile	64°
99.0	7	1	6	..	..	..	ductile	83
93.5[2]	2	..	1	1	..	..	moderately ductile	91
102.4	11	4	..	5	..	..	brittle	96
132.0	11	..	9	..	..	..	ductile	127
132.5	2	..	..	1	..	..	brittle	..
143.5[3]	2	1	..	..	..	..	brittle	137
144.8[4]	..	2	5	3	..	..	ductile	137
166.5	..	..	..	4	3	..	ductile	..
172.0	..	1	..	2	..	..	ductile	..
178.3[5]	..	..	3	5	..	..	ductile	175
194.0	..	..	..	10	..	1	ductile	..

It is interesting to note that the alloys which do not contain bismuth are ductile, while the alloys containing bismuth are brittle, unless they contain a large percentage of lead and little if any tin or cadmium.

SCHENECTADY, N. Y.

[1] Wood's metal, expands after cooling.
[2] Rose metal, expands after cooling.
[3] Combustible above melting point.
[4] Cadmium solder. Lowest melting alloy not containing the expensive bismuth.
[5] Tin solder.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY, No. 308.]

THE FALLACY OF DETERMINING ELECTRICAL CHARGE OF COLLOIDS BY CAPILLARITY.

BY A. W. THOMAS AND I. D. GARARD.

Received August 13, 1917.

The capillarity method for the determination of the sign of the electrical charge of colloids is fallacious. This method, proposed by Sahlbohm[1] and Fichter,[2] is recommended by Wo. Ostwald[3] under the name of "Capillary Analysis" as a convenient method of distinguishing between positively charged and negatively charged colloids. Due to its simplicity it is widely used by those who are primarily interested in colloids.

According to the authors of the method, negatively charged colloids ascend strips of filter paper which are dipped into their dispersions while positively charged colloids do not ascend, but coagulate on the paper a slight distance above the level of the dispersion into which the filter paper is dipping, and the explanation offered is that the filter paper, or cellulose, is negatively charged against water and hence an oppositely charged colloid will have its charge neutralized and precipitate on the paper while a like charged colloid will be unaffected and consequently climb up the paper by capillarity.

Our experience has verified the method in the cases of the negatively charged colloids—gold, platinum, arsenious sulfide, etc., as ordinarily prepared, which are *dilute*, and in the case of the positively charged colloids—hydrous ferric oxide when prepared in the *concentrated* form by the method of peptization of ferric hydroxide by ferric chloride.

We were led to investigate the method, however, by the conduct of a *dilute* hydrous ferric oxide sol which *ascended* filter paper strips. This sol had been prepared by the method of hydrolyzing ferric chloride by addition of a small amount of this salt to a large volume of boiling water.

Report of a few of our experiments, which are sufficient to condemn the "capillary analysis" method, follows.

Method.

Ten cc. of the colloidal dispersion to be tested were placed in a small (15 cc.) evaporating dish and a strip of filter paper (Schleicher and Schüll No. 597) about 1 cm. wide and 15 cm. long was suspended with the lower end dipping below the surface of the liquid, but not touching the dish. A glass case was placed over this outfit to prevent excessive evaporation, and to protect from drafts and dust. Observation of the height to which

[1] *Kolloidchem. Beihefte*, 2, 79–141 (1910).

[2] *Kolloid Z.*, 8, 1–2 (1911).

[3] "Handbook of Colloid Chemistry," p. 15.

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the dispersion ascended was made at the end of a suitable interval, generally 48 hours.

Inorganic Dispersions Used.

(I) **Hydrous Ferric Oxide Sol by Peptization Method** (a positive colloid).—This hydrosol was prepared by peptization of freshly precipitated ferric hydroxide with ferric chloride. 135 g. of ferric chloride were dissolved in 100 cc. of distilled water and small quantities (about 1 cc. at a time) of 3 *N* ammonium hydroxide solution were added, followed by shaking to allow the ferric hydroxide to "dissolve," that is, to be peptized by the excess of ferric chloride present. When by the slowness of peptization it was observed that nearly all of the iron was in the hydrosol condition, the dispersion was placed in collodion sacks, dialyzed for 6 hours against running tap water and then against distilled water for 156 hours, changing the water twice daily. By this time the dialysate gave but a faint test for chloride.

Analysis of this hydrosol showed a content of 0.0143 g. Fe_2O_3 and 0.0018 g. Cl per cc.

(II) **Hydrous Ferric Oxide Sol by Hydrolysis Method** (a positive colloid).—This hydrosol was prepared by hydrolysis of ferric chloride. Five cc. of a 10% ferric chloride solution were boiled with 500 cc. of distilled water for 10 minutes and then dialyzed against distilled water for 5 days.

(III) **Hydrous Chromic Oxide Sol** (a positive colloid).—This hydrosol was prepared from chromic chloride in a manner similar to (I), described above. It was dialyzed against running water for 34 hours and then against distilled water for 48 hours.

Upon analysis it showed 0.0012 g. Cr_2O_3 per cc. and but a faint trace of chloride present.

(IV) **Arsenious Sulfide Sol** (a negative colloid).—A saturated solution of arsenious acid, prepared by boiling an excess of arsenious oxide with distilled water and filtering, was saturated with hydrogen sulfide by passing the gas through it for 12 hours and shaking frequently. A very concentrated, though clear, hydrosol was obtained. It was not dialyzed for fear of coagulation.

Analysis showed it to contain 0.013 g. As_2S_3 per cc.

(V) **Antimony Sulfide Sol, Undialyzed** (a negative colloid).—2.5 g. of potassium antimonyl tartrate (tartar emetic) were dissolved in 500 cc. of distilled water and the solution was saturated with hydrogen sulfide.

(VI) **Antimony Sulfide Sol, Dialyzed.**—400 cc. of (V) were dialyzed for 3 days against distilled water, changing the water twice daily.

This hydrosol contained 0.0017 g. Sb_2S_3 per cc.

(VII) **"Molybdenum Blue" Sol** (a negative colloid).—This hydrosol

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was prepared according to Biltz.[1] It was dialyzed for several days against distilled water.

Experimental.

From the observation which suggested this investigation, *i. e.*, that a *dilute* ferric oxide hydrosol ascends filter paper strips, we suspected that dilution of the sol is the cause of the ascent since all other iron oxide hydrosols which had been used formerly and which did not ascend filter paper strips, were quite *concentrated*. The concentrated sols were prepared by the "Peptization" method while the dilute sol was a result of the "Hydrolysis" method of preparation.

The effect of dilution upon capillarity was accordingly studied with the results given below.

HYDROSOL (I).

Conc. of sol	1.0[2]	0.1[3]	0.05[3]	0.02	0.002	0.001
Ascent in cm. after 48 hrs	1	1	1	5	5	5

Hydrosol (II), even when undiluted, readily ascended to the tops of the filter paper strips.

It is evident, therefore, that the positively charged colloid, hydrous ferric oxide, will ascend a strip of filter paper by capillarity if it is sufficiently dilute.

Since Miss Sahlbohm[4] noted that an incompletely dialyzed positive hydrosol would ascend a strip of filter paper, we tried the effect of addition of electrolyte to the ferric oxide sol. The concentrations of electrolyte cited below refer to the final concentration of the electrolyte in the mixture.

EFFECT OF FERRIC CHLORIDE ON HYDROSOL (I).

Conc. of sol	0.5	0.5	0.5	0.5	0.05	0.05	0.05	0.05	0.05
Conc. of $FeCl_3$	0	0.001 *M*	0.01 *M*	0.1 *M*	0	0.0001 *M*	0.001 *M*	0.01 *M*	0.1 *M*
Ascent in cm. after 48 hrs	1	1	1	5	1	2.5	3.5	7	8.5

Note that the capillary ascent was forced by adding ferric chloride to 0.1 *M* concentration to the fairly concentrated sol (0.5) and when the sol was ten times dilute (but still concentrated enough so that it would not ascend), it ascended when as little as 0.0001 *M* ferric chloride was present.

EFFECT OF HYDROCHLORIC ACID ON HYDROSOL (I).

Conc. of sol	0.05	0.05	0.05	0.05
Conc. of HCl	0	0.0001 *M*	0.001 *M*	0.01 *M*
Ascent in cm. after 48 hrs	2	5	4	5

[1] "Laboratory Methods of Inorganic Chemistry," 1909, p. 39.

[2] This means that the sol was used undiluted.

[3] These numbers mean that to each 0.1 cc. of sol (I), 0.9 cc. of distilled water was added, and to 0.05 cc. of (I), 0.95 cc. of water was added, and so on.

[4] *Kolloidchem. Beihefte*, 2, 79 (1910).

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Analysis of the wetted part of the strip of paper above the level to which the sol had ascended, showed the presence of hydrochloric acid.

Neutral electrolytes did not cause the ferric oxide sols to ascend, with the possible exception of ammonium chloride, which, in concentrations of 0.01 molar, seemed to cause a slight ascent of the sol of 0.05 concentration. This is attributed to the fact that this salt is slightly acid in reaction. Hence we may state that electrolyte of acid reaction, or the presence of hydrogen ion will cause a positive colloid, such as ferric oxide hydrosol, to ascend filter paper strips.

EFFECT OF DILUTION UPON HYDROSOL (III). CHROMIC OXIDE.

Conc. of sol	1	0.8	0.6
Ascent in cm. after 48 hrs	2	5	6

Since the color of this sol was quite faint, we had difficulty in detecting the height of ascent. By moistening the papers with dilute alkali and immersing in bromine vapors, oxidation to chromate resulted in a yellow color which was plainly visible with the concentrations given above, but could not be used with concentrations lower than the 0.6 given above.

Note that this positive colloid also ascends when sufficiently dilute.

The next step in the proof of the fallacy of the method of "capillary analysis" was to prepare some negative colloids so concentrated that they would not run up the filter paper. We succeeded in our attempt as shown by the following record:

EFFECT OF DILUTION UPON ARSENIOUS SULFIDE HYDROSOL (IV).

Conc. of sol	1	0.1	0.05
Ascent in cm. after 96 hrs	2	4	12

The above recorded heights were reached in 24 hours and did not alter during the additional 72 hours. Distinct coagulum lines were formed on the strips at the heights noted, just as in the case of the ferric oxide hydrosol. Note in the directions of preparation, given earlier in this report, that we took special care to make this sol as concentrated as possible. When arsenious sulfide sols are made by the ordinary method of mixing equal volumes of saturated arsenious acid solution and hydrogen sulfide water, they readily climb the paper strips since they are so dilute.

EFFECT OF DILUTION UPON ANTIMONY SULFIDE HYDROSOL (VI).

Conc. of sol	1	0.5	0.1
Ascent in cm. after 48 hrs	0.5	2	8

After much longer standing the above sols did not climb any further.

In the presence of 0.02 *M* sodium hydroxide, the concentrated one ascended 5 cm. Hence hydroxyl ion will cause a negative colloid to ascend by capillarity just as hydrogen ion does in the case of the positive colloids.

EFFECT OF DILUTION UPON ANTIMONY SULFIDE HYDROSOL, UNDIALYZED (V).

Conc. of sol	1	0.5
Ascent in cm. after 48 hrs	0.5	2

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Note that this negative colloid did not ascend the papers as far as the positive colloid (I) did.

EFFECT OF DILUTION UPON "MOLYBDENUM BLUE" HYDROSOL (VII).

Conc. of sol.....	Original sol.	Concd. 60 times
Ascent in cm. after 48 hrs.....	15	4.5

It is evident from these experiments that the ascent of the filter paper strips is a function of the concentration of the colloid even when it is negatively charged.

Another interesting observation which was made, and which constitutes another argument against the validity of the method of capillarity, was that if the papers up which the sol had not climbed, and upon the lower end of which there was a coagulation rim of the sol, were shaken so as to wet above this line of coagulation, or if the paper were permitted to cling to the side of the glass vessel containing the sol, then the sol would ascend for several centimeters regardless of the nature of its charge.

Capillary Conduct of Some "Colloidal" Dyestuffs.

Since the preparation of very concentrated negative hydrosols, in the absence of an emulsoid or protective colloid, seemed to be rather difficult and due to the fact that we desired to try more than the three negative sols reported above, our attention was turned to those dyestuffs which are described as colloids.

We selected two so-called positive colloidal dyes[1]—Bismarck brown and methylene blue—and two so-called negative colloidal dyes—eosin and fuchsin, and made saturated aqueous dispersions of them. They all ascended filter paper strips alike, even when ten times diluted with water. Since there was a possibility of electrolyte impurities affecting the conduct of these dyes, they were then dialyzed to remove the electrolytes, but with the result that the dyes themselves diffused through the collodion dialyzing membranes. Hence the colloidal nature of these dyes is very doubtful and a revision of the generally accepted statements concerning their colloidal nature is suggested.

Effect of the Nature of Filter Paper on Capillarity.

Since Miss Sahlbohm found that a positively charged colloid would climb an acid-washed filter paper, it was considered interesting to compare the capillarity ascent of a colloid upon different kinds of filter paper. Several grades of Whatman and of Schleicher and Schüll papers were tried, using ferric oxide hydrosol (I) of different dilutions, with the result that a different height of ascent was obtained with a given dilution of (I) for each kind of paper. This is another objection to the method. Two specimens of the same grade of paper, one being much older than the other, gave discordant results also.

[1] Burton, "Physical Properties of Colloidal Solutions," 1916, p. 126.

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The last objection is not needed in the condemnation of the method, however, since it is very plain that there is no relation between the sign of the electrical charge of a colloid and its capillarity ascent of a strip of filter paper which may be immersed in it.

The height of ascent is dependent upon the dilution of the sol, the presence of electrolyte, the external conditions such as surrounding atmosphere, and the nature of the filter paper used.

We believe that the method was innocently proposed due to the result of the peculiar circumstance that the positive colloids which the originators of the methods used were concentrated while their negative colloids were dilute. In fact it is very difficult to obtain the negative colloids in a concentrated state in the absence of a protective colloid. It is impossible to get the colloidal noble metals concentrated, we succeeded only with the sulfides.

NEW YORK CITY.

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF ILLINOIS. PUBLICATION NO. 29.]

THE EQUIVALENT CONDUCTANCE OF ELECTROLYTES IN DILUTE AQUEOUS SOLUTION.

I. THE WATER CORRECTION.

BY EDWARD W. WASHBURN.

Received September 25, 1917.

CONTENTS.—1. Introduction to the Series. 2. The Magnitude and Nature of the Water Correction. 3. The Stability of Conductivity Water in Contact with the Atmosphere. 4. The Carbonic Acid Concentration and the Acidity of Conductivity Water. 5. The Relation between Specific Conductance and Degree of Ionization. 6. Calculation of the Carbonic Acid Metathesis Correction. 7. Salts of Strong Acids and Bases. 8. Influence of Saline Impurities upon the Metathesis Correction. 9. Salts of Weak Acids and Bases. 10. Salts of Higher Valence Types. 11. Acids and Alkalies.

1. Introduction to the Series.—Any theoretical interpretation, in terms of the Ionic Theory, of the properties and behavior of solutions containing electrolytes involves as one of its essential factors a knowledge of the degrees of ionization of the electrolytes present in the solution. The most reliable method of determining the degree of ionization, α, of a uni-univalent electrolyte at the concentration C is by means of the relationship $\alpha = \Lambda_c/\Lambda_0$ where Λ_c is the *true equivalent conductance* of the electrolyte at the concentration C (corrected, if necessary, for viscosity influences) and Λ_0 is its *true equivalent conductance* at zero concentration.

By *true equivalent conductance* is meant the equivalent conductance of the electrolyte at the concentration in question, when the solution contains no ions other than those resulting from the direct ionization of the elec-

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trolyte itself. The *measured equivalent conductance* differs in general from the true equivalent conductance not only directly, because of the presence of other ions (H^+ ion and OH^- ion from the water and other ions from impurities dissolved in the water), but also indirectly due to metathesis which occurs between the electrolyte and the water (hydrolysis) and between the electrolyte and the impurities present in the water.

The value of Λ_0 is usually obtained by extrapolating, to $C = 0$, some empirical function which is found to represent more or less satisfactorily the observed relation between Λ_c and C over at least the lower portions of the concentration range. The lowest concentration to which any observer has hitherto found it practicable to push conductivity measurements is $C = 0.0001\ N$. This limitation of the concentration range open to measurement is due to the magnitude of the "water correction" in the very dilute solutions and the uncertainty involved in applying it.

Conductivity water which is approximately stable in contact with the atmosphere ("equilibrium water") has a specific conductance of the order of magnitude of 1×10^{-6} reciprocal ohms, due to the impurities (chiefly carbon dioxide) which it dissolves from the air. The direct "water correction" which must therefore be made to the measured value of the conductivity of a dilute salt solution may amount at $C = 0.0001\ N$ to as much as *10* %, at $C = 0.00001\ N$ to as much as *100* %, and at $C = 0.000001\ N$ to as much as *1000* % of the conductivity of the salt itself, and aside from the magnitude of the correction the proper method of applying it is rendered uncertain in many cases owing to our lack of knowledge as to the exact natures and amounts of the impurities present in the conductivity water, as well as to lack of sufficient constancy in the conductivity of the water during the time which is required to prepare and measure the conductivity of the salt solutions.

The Λ_0 values in use at present have, consequently, been obtained by extrapolation from conductivity data which in the most favorable cases do not extend below $C = 0.0001\ N$ and which in many cases stop at about $C = 0.001\ N$. The values of Λ_0 deduced by different observers from the same conductivity data are, therefore, almost as numerous as the different functions which have been proposed for representing the data over the range open to measurement; ranging, for example, in the case of KCl at 18° from $\Lambda_0 = 127.9$ (Muller and Romann[1]), $\Lambda_0 = 128.3$, (Kraus and Bray) and $\Lambda_0 = 128.5$, (Wegscheider[2]), to $\Lambda_0 = 130.0$ (Kohlrausch, Noyes and Falk). Now unless the Λ_0 value for a salt can be determined with a certainty of at least 0.01 to 0.02% we cannot hope to obtain any information concerning questions which involve a knowledge of the concentration of the un-ionized molecules of strong electrolytes in dilute solu-

[1] Muller and Romann, *Compt. rend.*, **157**, 400 (1913).

[2] *Z. physik. Chem.*, **69**, 624 (1909).

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tions, such questions, for example, as the behavior of strong electrolytes with respect to the requirements of the Mass Action law.

About eight years ago the writer became convinced that the *only possible way* of securing an unequivocal answer to these much discussed questions was to obtain accurate conductivity data in the region of concentration below 0.0001 N and that in spite of the great difficulties which such an investigation presented, the questions at stake were of sufficient importance to make the attempt worth while. Accordingly, with the aid of a grant from the Bache Fund of the National Academy of Sciences, the investigation was begun in 1911.

The first part of the problem consisted in so developing and perfecting the Kohlrausch method for measuring electrolytic conductance that an accuracy of better than 0.01% could be obtained in measuring the conductance of very pure water and of these very dilute solutions. With the valued assistance of J. E. Bell and Karr Parker this part of the problem was so successfully solved that the resistance measurement itself can be made with practically no error whatever. This part of the work has already been partly published.[1]

The second part of the problem resolved itself into the preparation, in large quantities, of conductivity water which should be almost chemically pure and the preservation of the purity of this water during the operations of preparing and measuring the conductivity of the solutions. The methods by which this was successfully accomplished are described in the third paper of this series.

The problem of the correct method of extrapolating in order to obtain a reliable Λ_0 value is discussed in the second paper, while the fourth paper describes some new laws which have been established as a result of the investigation and presents a revised table of Λ_0 values computed by means of a new rule with the aid of which it is possible to calculate Λ_0 values from a single Λ_c value, for a sufficiently dilute solution.

2. The Magnitude and Nature of the "Water Correction."—The subject of the amount and nature of the impurities in conductivity water and the method of applying the "water correction" has been discussed by many investigators. A comprehensive review of previous work in this field and a new discussion of the problem has been given within the last year in a series of papers by James Kendall.[2] The recent publication of Kendall's papers renders it unnecessary to include here a review of the previous work on this topic and in fact all further discussion of the question would be omitted here were it not for the fact that the writer's conclusions are, in several important respects, at variance with those reached by Ken-

[1] THIS JOURNAL, **35**, 177 (1913); **38**, 2431 (1916); **39**, 235 (1917); and one additional paper by Washburn and Parker, yet to be prepared for publication.

[2] THIS JOURNAL, **38**, 1480 and 2460 (1916); **39**, 9 (1917).

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dall. A sufficient discussion of the subject will therefore be presented to make clear the writer's views on the disputed points and the reasons therefor, as well as to present certain derivations and equations which will be employed in the subsequent papers of this series.

TABLE I.

Illustrating the Relative Magnitudes of the "Water Correction" in the Case of Conductivity Water of Different Degrees of Purity.

Concentration of KCl. Mol per liter.	Specific conductance of the salt $\times 10^6$.	Magnitude of the water correction expressed in per cent. of the conductance of the salt; for water having the specific conductance.		
C.	$L_E \times 10^6$.	1×10^6.[1]	0.06×10^6.[2]	0.04×10^6.[3]
0.000001	0.129	886.0	31.0	24.0
0.00001	1.296	44.0	4.4	3.0
0.0001	12.90	7.7	0.46	0.31
0.001	127.3	0.78	0.047	0.031
0.01	1224.0	0.082	0.0049	0.003
0.1	11200.0	0.009	0.00054	0.00036

The data in Table I illustrate the relative magnitudes of the "water correction" for different grades of conductivity water in the case of potassium chloride. The figures in the third column show clearly why it is impracticable to extend conductivity measurements below 0.0001 N when measurements are carried out in contact with the atmosphere, as long as the slightest uncertainty exists as to the exact value of the "water correction." The figures in Col. 5 illustrate the magnitude of the "water correction" for practically chemically pure water. A comparison between the values in Cols. 4 and 5 brings out the interesting fact that as far as salts of strong acids and bases are concerned there is practically no advantage to be gained in working with water which has a specific conductance lower than 0.06×10^{-6} since the magnitude of the "water correction" with this water is substantially the same as that for chemically pure water. Water for which this statement is true will hereafter be referred to as "ultra-pure conductivity water," a term suggested by Kendall.

Kendall in his discussion of this point makes the statement[4] that if it were possible to employ chemically pure water in conductivity work, "then it is obvious that we should never need to apply to our results any

[1] "Equilibrium water," *i. e.*, water saturated with carbon dioxide under atmospheric conditions. This is the grade of water employed in obtaining the most reliable conductivity data at present available.

[2] Water which can be prepared and kept in an atmosphere of purified air.

[3] Water obtained in small quantities by Kohlrausch and Heydweiller; practically chemically pure.

[4] THIS JOURNAL, 38, 2460 (1916); 39, 9 (1917).

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'water correction' at all." This statement is somewhat inaccurate since with such water the correction at 0.0001 N would still amount to about 0.3% and that at 0.00001 N to about 3%. The advantage to be gained in working with the ultra-pure water is not the entire elimination of a "water correction" but rather the elimination of all uncertainty as to the correct method of applying such a correction.

There are two conceivable methods of obtaining reliable conductance data in very dilute solutions: one of these is to employ, for the conductivity measurements, water of a very high degree of purity under such conditions that no contamination can take place during the work; the other is to determine the amounts and nature of the impurities present in conductivity water in equilibrium with the atmosphere and then to calculate with the aid of the Mass Action law the corresponding metathesis corrections. Kendall considers the first method impracticable stating[1] that

"In order to do this, however, it would be essential to carry out all manipulations, preparation of solutions and measurements of conductivities in evacuated vessels. This is a feat which has been frequently attempted, but owing to the extraordinary experimental difficulties involved, not yet been successfully concluded."

The great difficulties associated with preparing and working with the ultra-pure water were thoroughly appreciated by the writer before the present investigation was started and this appreciation did not materially diminish during the first five years of the work. In spite, however, of the obvious difficulties of applying this method to the solution of the problem the writer is convinced that it is *the only one* of the two which is capable of yielding reliable results.

The second method—the one preferred by Kendall—does not seem to the writer capable of solving the problem at all, for the following reasons: first, because although undoubtedly most of the conductance of conductivity water in contact with the atmosphere is caused by carbon dioxide, the evidence brought together by Kendall does not demonstrate by any means that all of the conductance is due to this substance. In fact some of his evidence, as will be pointed out below (Sec. 11), shows, it seems to the writer very definitely that the conductance cannot all be due to carbon dioxide; second, because, as will be shown below, it is essential that the conductance of such water shall be maintained constant to 0.01% during the operations of preparing and measuring the conductivity of the solutions, a feat which would be quite as difficult as that of preparing and working with ultra-pure water.

3. The Stability of Conductivity Water in Contact with the Atmosphere.—If conductivity water in equilibrium with the atmosphere is employed, the "water correction" for a 0.00001 N solution amounts to about 40 % in case of potassium chloride and to about 100 % in case of

[1] THIS JOURNAL, 39, 9 (1917); 38, 2460 (1916).

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LiCl. In order, therefore, to avoid introducing an error of more than 0.01% when applying the "water correction" at this concentration, it would in general be necessary to maintain the conductivity of the water itself, constant, to within about 0.01% of its initial value. Now, it is true that when very pure water is allowed to stand in contact with the atmosphere it absorbs carbon dioxide and its conductivity rises at first rapidly and then more slowly until it reaches a maximum value somewhere between 0.8 and 1.0×10^{-6} depending upon the atmospheric conditions of the locality. This conductivity corresponds *approximately* to a saturated solution of carbon dioxide under atmospheric conditions[1] and such conductivity water is referred to in this paper as "equilibrium water."

If solutions are to be made up and handled in contact with the atomsphere, the logical procedure is, as repeatedly pointed out by Kohlrausch, to employ water whose conductivity does not change in contact with the atmosphere, rather than to employ a purer water than this. It by no means follows, however, that the conductances of solutions below 0.0001 N could be accurately determined by employing such water even though the only impurity in it were carbon dioxide and the method of applying the "water correction" not open to any question. Before such a conclusion could be justified it would first be necessary to demonstrate that the conductivity of the "equilibrium water" is itself constant to the required degree of precision under working conditions.

Now the variability of the conductivity of "equilibrium water" will of course depend upon local conditions and experimental methods, so that a general exact quantitative answer to this question cannot be given. The best that can be done is to present some data showing what the magnitude of the variation has amounted to in some specific instances.

This question was definitely investigated by Kohlrausch. His investigations[2] extended over a whole week and show very clearly that there is considerable variability in the conductivity of such water even when air from outdoors is bubbled through it on different days. Moreover, he states that if a current of air freed from carbon dioxide is drawn through equilibrium water so as to reduce its conductivity from 1.0 to 0.6 it does not again attain its original value on contact with the atmosphere. Furthermore, he points out that air taken from the room exhibits a great and erratic variability. The presence of a man or of a gas burner in the room can be easily detected from its influence upon the conductance of the water.

Kohlrausch's results are in accordance with the experience of the writer.

[1] Kohlrausch, *Gesammelte Abhandl.*, 2, 871; Kendall, THIS JOURNAL, 38, 2464 (1916).

[2] *Gesammelte Abhandl.*, 2, 996.

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In this connection the following experiment, carried out in the writer's laboratory, may be cited:

Conductivity water was collected hot in a three-liter quartz flask fitted with electrodes and with means for passing air through the water without permitting the water to come in contact with anything but quartz or platinum. Some of the same water was also placed in a bottle which was connected to the quartz flask in such a way that all the air which entered the quartz flask first bubbled through the water in the bottle. Air from the laboratory[1] was first drawn through the water in the quartz flask which was maintained at a temperature of 18° in an oil thermostat.

After about 24 hours of this treatment the water had a specific conductance of 0.836×10^{-6} reciprocal ohms, but did not exhibit any tendency to become constant to a very high degree or precision. It was therefore decided to draw the air from out of doors. The experiment was therefore continued with filtered outdoor air passing through the system. The following series of results was obtained, the air being shut off temporarily each time while the conductance measurement was made:

Time.	$L \times 10^6$.	Time.	$L \times 10^6$.
3.20 P.M.	0.836	8.20 A.M.	0.846
3.22 P.M.	Out of door air introduced	8.22 A.M.	Air supply shut off
3.50 P.M.	0.816	8.26 A.M.	0.848
4.10 P.M.	0.813	9.10 A.M.	0.855
4.40 P.M.	0.810	9.11 A.M.	Flask shaken
6.35 P.M.	0.797	9.15 A.M.	0.860
7.10 A.M.	0.840	9.16 A.M.	Flask shaken again
7.35 A.M.	0.846	9.17 A.M.	0.8608
8.00 A.M.	0.850	9.26 A.M.	0.8648

It is evident from the above data that there is no tendency for the water to reach a sufficiently constant conductance with the air passing through it, even when, as in this experiment, the air is subjected to a preliminary washing with conductivity water.

The writer is unable, therefore, to accept the conclusion that in attacking the problem of the conductivity of very dilute solutions the most logical procedure is to employ "equilibrium water" and to compute an exact water correction on the assumption that the conductivity is due solely to carbon dioxide. It seems to the writer that one of the chief errors in any such conclusion arizes from the tacit assumption that it is more difficult to maintain, to the necessary degree of precision, the purity of "ultrapure conductivity water" than it is to maintain that of "equilibrium water." The entrance of a given amount of carbon dioxide into the con-

[1] The room in which the experiment was conducted was a laboratory especially located and designed to insure a minimum contamination of the air. No gas flames were in the neighborhood and no person was in the room except for the brief periods necessary for making the measurements, during which the observer was shut up in a telephone booth.

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ductivity water produces, it is true, an enormously greater *relative* change in the conductivity of the "ultra-pure water" as compared with that produced in the conductivity of the "equilibrium water," but the *absolute* change in conductivity will be of approximately the same order of magnitude in both cases[1] and it is the *absolute change only, which is here involved.* It should not, therefore, be much if any, more difficult to protect the ultra-pure water from contamination than it would be similarly to protect the equilibrium water from an equally harmful variation in its conductance.

4. The Carbonic Acid Concentration and the Acidity of Conductivity Water.—If the only impurity present in conductivity water is carbon dioxide, the total concentration, C_{CO_2}, of this substance can be calculated from the relation

$$C_{CO_2} = \frac{[H^+]^2_W}{K_I} + [H^+]_W - \frac{K_W}{K_I} - \frac{K_W}{[H^+]_W} \qquad (1)$$

where K_I and K_W are defined by the Equations 17 and 19. The hydrogen-ion concentration, $[H^+]_W$, will be given by the expression

$$[H^+]_W = \frac{L_W \times 10^3}{2\Lambda_{H_2CO_3}}\left[1 + \sqrt{1 - \frac{4\Lambda_{H_2CO_3}(\Lambda_{OH} - \Lambda_{HCO_3})}{\Lambda^2_{H_2O}}\left(\frac{L_P}{L_W}\right)^2}\right] \qquad (2)$$

where L_W is the specific conductance of the conductivity water and L_P is the specific conductance of chemically pure water at the same temperature. For conductivity water in contact with the atmosphere Equation 2 reduces to the simple form

$$[H^+]_W = \frac{L_W \times 10^3}{\Lambda_{H_2CO_3}}. \qquad (3)$$

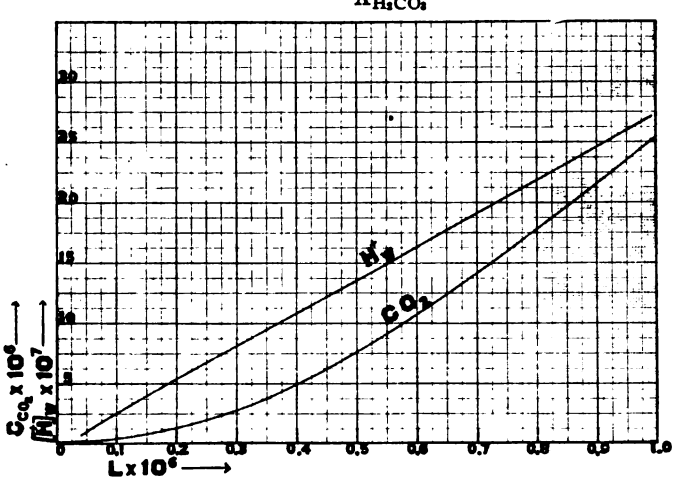

Fig. 1.—Illustrating the relation between the conductance of conductivity water and (*a*) the carbon dioxide concentration, (*b*) the hydrogen-ion concentration.

[1] Cf. curve $[H^+]_w$ in Fig. 1.

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Graphs showing the variation of C_{CO_2} and of $[H^+]_W$ with L_W at 18° are shown in Fig. 1.

5. The Relation between Specific Conductance and Degree of Ionization.—If a solution containing C equivalents of a salt BA per liter could be prepared with water possessing zero conductance, then the specific conductance L_E of this solution would be

$$1000\, L_E = \alpha C\,(\Lambda_B + \Lambda_A) \qquad (4)$$

where α is the degree of ionization of the salt and Λ_B and Λ_A are the equivalent conductances of its two ions in the solution in question. In order, therefore, to calculate the degree of ionization of a salt from conductance data, it is the quantity L_E, that is, the *true specific conductance* of the salt, which must be determined.

Now in practice it is, of course, not possible to employ water possessing zero conductance. Consequently, the measured specific conductance of the salt solution will not be its true specific conductance. If the specific conductance of the conductivity water is L_W, then the measured specific conductance L_S of the resulting salt solution will be

$$L_S = L_W + L_E - \Delta L \qquad (5)$$

where ΔL represents the total amount by which the *two conductances* L_W and L_S are decreased as a result of the metathetical processes which occur when the salt is dissolved in the water. These metathetical processes bring about a *decrease* in the total conductance owing to the formation of the un-ionized molecules BOH, HA, and $BHCO_3$, provided that carbon dioxide is the only impurity in the conductivity water which needs to be reckoned with. The purer the conductivity water and the higher the concentration of the salt, the smaller will be the percentage correction involved in the quantity ΔL. Even in the case of absolutely pure water, however, this metathesis correction would be very large in the case of salts of weak acids and bases.

6. Calculation of the Carbonic Acid Metathesis Correction.—*The General Equations.*—From Equation 5 we have

$$\Delta L = L_W + L_E - L_S \qquad (6)$$

or substituting

$$1000\,\Delta L = (\Lambda_H[H^+]_W + \Lambda_{OH}[OH^-]_W + \Lambda_{HCO_3}[HCO_3^-]) + (\Lambda_B\alpha C + \Lambda_A\alpha C)$$
$$- (\Lambda_H[H^+]_S + \Lambda_{OH}[OH^-]_S + \Lambda_{HCO_3}[HCO_3^-]_S) + \Lambda_B[B^+]_S + \Lambda_A[A^-]_S \qquad (7)$$
$$= \Lambda_H\Delta_H + \Lambda_{OH}\Delta_{OH} + \Lambda_{HCO_3}\Delta_{HCO_3} + \Lambda_B\Delta_B + \Lambda_A\Delta_A \qquad (8)$$

where

$$\Delta_H = [H^+]_W - [H^+]_S, \qquad (9)$$
$$\Delta_B = \alpha C - [B^+]_S, \text{ etc.} \qquad (10)$$

In the above expressions a bracketed symbol indicates the equivalent

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concentration of the bracketed quantity and the subscript following the bracket indicates whether it is the concentration in the conductivity water (w) or in the salt solution (s) which is intended. The Δ's for the separate ions evidently indicate the decreases in the concentrations of the ions in question which result from the metatheses. The values of these individual ion Δ's and hence also the value of ΔL, the total metathesis correction, can be computed for all possible cases from the simultaneous solution of the following set of equations:

$$\frac{[B^+][A^-]}{[BA]} = K_S \quad (11) \qquad [BA] = \frac{[B^+][A^-]}{K_S} \quad (12)$$

$$\frac{[H^+][A^-]}{[HA]} = K_A \quad (13) \qquad [HA] = \frac{[H^+][A^-]}{K_A} = [H^+]\frac{\alpha C}{K_A} \quad (14)$$

$$\frac{[B^+][HCO_3^-]}{[BHCO_3]} = K_C \quad (15) \qquad [BHCO_3] = \frac{[B^+][HCO_3^-]}{K_C} = [HCO_3^-]\frac{\alpha C}{K_C} \quad (16)$$

$$\frac{[H^+][HCO_3^-]}{[H_2CO_3]} = K_I \quad (17) \qquad [HCO_3^-] = \frac{K_I[H_2CO_3]}{[H^+]} \quad (18)$$

$$[H^+][OH^-] = K_W \quad (19) \qquad [BOH] = \frac{K_W \alpha C}{[H^+]K_B} \quad (20)$$

$$[H_2CO_3] + [HCO_3^-] + [BHCO_3] = C_{CO_2} \quad (21)$$

$$[H_2CO_3] + \frac{K_I[H_2CO_3]}{[H^+]} + \frac{K_I[H_2CO_3]\alpha C}{[H^+]K_C} = C_{CO_2} \quad (22)$$

$$[H_2CO_3] = C_{CO_2} \div \left(1 + \frac{K_I}{[H^+]}\left(1 + \frac{\alpha C}{K_C}\right)\right) \quad (23)$$

$$[HCO_3^-] = K_I C_{CO_2} \div \left([H^+] + K_I\left(1 + \frac{\alpha C}{K_C}\right)\right) \quad (24)$$

$$[BHCO_3] = K_I C_{CO_2} \alpha C \div K_C\left([H^+] + K_I\left(1 + \frac{\alpha C}{K_C}\right)\right) \quad (25)$$

$$[B^+] + [BA] + [BHCO_3] + [BOH] = C \quad (26)$$

$$[A^-] + [BA] + [HA] = C \quad (27)$$

$$[H^+] + [B^+] = [HCO_3^-] + [A^-] + [OH^-] \quad (28)$$

The general solution of this set of equations will not be discussed here as only the special case of a salt of a strong acid and base will be required in what follows. For this case the solution of the equations can be considerably simplified as the metathesis correction will obviously be very small.

7. The Carbonic Acid Metathesis Correction for Salts of Strong Acids and Bases.—For this case we can write

$$K_A = K_C = K_S = \frac{\alpha^2 C}{1 - \alpha}. \quad (29)$$

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Making this substitution and solving the above set of equations we find the following sufficiently exact expressions:

$$\Delta_H = [H^+]_W - [H^+]_S =$$

$$\frac{\left[1 - \alpha - \frac{\{[H^+]_W(1-\alpha) + \alpha\Delta_H\}\alpha}{K_I + \alpha([H^+]_W - \Delta_H)}\right]\left([H^+]_W - \frac{K_W}{[H^+]_W}\right)}{2 + \left[\alpha + \frac{\{[H^+]_W(1-\alpha) + \alpha\Delta_H\}\alpha}{K_I + \alpha([H^+]_W - \Delta_H)}\right]\left(\frac{K_W}{[H^+]^2_W} - 1\right) - \frac{\Delta_H}{[H^+]_W}} \quad (30)$$

from which Δ_H can be obtained by a series (three) of approximations, $[H^+]_W$ being given by Equation 3 and α being obtainable from Table VII;

$$\Delta_B = \Delta_A = \frac{(1-\alpha)[H^+]_S}{2-\alpha}\left[1 - \frac{\Delta_B}{\alpha C}\right] =$$

$$\text{(approx.)}\ \frac{(1-\alpha)([H^+]_W - \Delta_H)}{2-\alpha} \quad (31)$$

$$\Delta_{HCO_3} = \frac{[K_I(1-\alpha) - \alpha\Delta_H]([H^+]^2_W - K_W)}{[K_I + \alpha([H^+]_W - \Delta_H)][H^+]_W} \quad (32)$$

and

$$\Delta_{OH} = \frac{-K_W\Delta_H}{[H^+]^2_W - [H^+]_W\Delta_H}. \quad (33)$$

By means of these equations and Equation 7 the value of ΔL, the total metathesis correction, can now be calculated for any uni-univalent salt of a strong acid and base.

For conductivity water in contact with atmosphere Δ_{OH} will be entirely negligible and we can write Equation 8 in the form

$$1000\,\Delta L = (\Lambda_H + \Lambda_{HCO_3})\,\Delta_H + (\Lambda_B + \Lambda_A)\,\Delta_B \quad (34)$$

or

$$1000\,\Delta L = \Lambda_{H_2CO_3}\Delta_H + \Lambda_{BA}\Delta_B. \quad (35)$$

This shows that the total carbonic acid metathesis correction for conductivity water in contact with the atmosphere can be regarded as made up of two parts, one part representing the decrease in the conducting power of the carbonic acid, the other the decrease in the conducting power of the dissolved salt.

The value of the metathesis correction expressed in terms of per cent. of the conductance of the salt will be

$$P_M = \frac{100\Delta L}{L_E} = \frac{\Lambda_{H_2CO_3}}{10L_E}\Delta_H + \frac{\Lambda_{BA}}{10L_E}\Delta_B \quad (36)$$

$$= \frac{\Lambda_{H_2CO_3}}{\Lambda_{BA}} \times \frac{100\Delta_H}{\alpha C} + \frac{100\Delta_B}{\alpha C} = P_I + P_S. \quad (37)$$

Curve A in Fig. 2 shows values of $P_I \times \Lambda_{BA}/\Lambda_{H_2CO_3}$ as a function of C, for "equilibrium water" at 18°. In order, therefore, to find the value of the

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metathesis correction due to the decrease in the conducting power of the carbonic acid, we have only to multiply the abscissa of the desired point on Curve A by the ratio $\Lambda_{H_2CO_3}/\Lambda_{BA}$. Thus for example, for a 0.0001 N solution of KCl at 18° this part of the metathesis correction would be

$$P_I = 0.54\ 353/129 = 0.0015\%.$$

Curves B and E in the same figure show, directly, values of P_S (in thousandths of a per cent.) as a function of C. Curve E is simply the lower portion of Curve B with the ordinate scale magnified 100-fold. From Curves A and B it is evident that the total metathesis correction increases with dilution and approaches a constant limiting value at high dilutions. Curve D shows the *total* metathesis correction, P_M, (in thousandths of a per cent.) as a function of the concentration in the case of KCl at 18°. The correction amounts to only 0.004% at 0.003 N and increases with dilution at first gradually and then more rapidly, reaching a limiting value of 0.016 % at high dilutions.

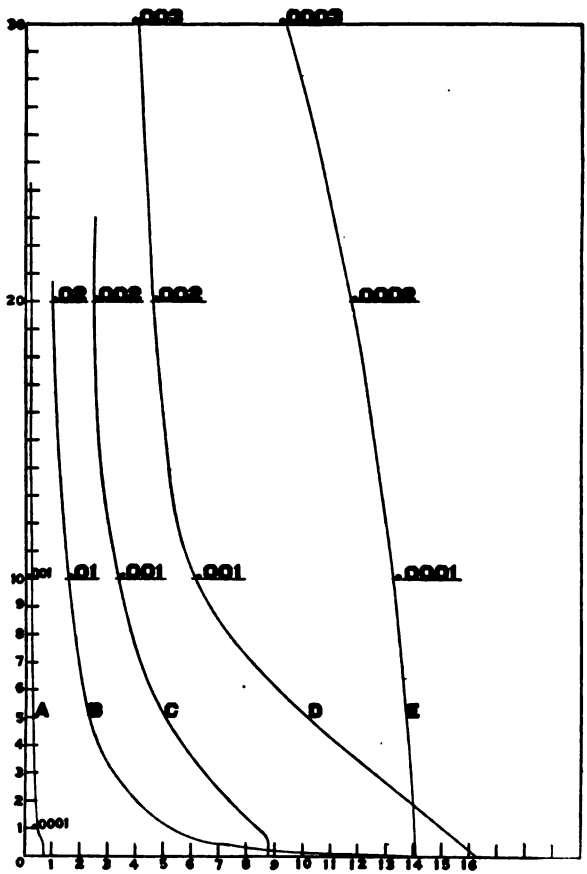

Fig. 2.—Curves illustrating the metathesis corrections for conductivity water. The abscissa scale represents thousandths of a per cent. in the case of Curves A, B, D and E, and hundredths of a per cent. in the case of Curve C. The ordinate scales represent concentration of the electrolyte and are indicated on each curve.

Owing to the fact that P_I is such a small part of the total correction P_M, an approximate expression may be substituted for its influence without significant loss of accuracy. From a study of Curves A, B, and D, and the equations upon which they are based, we find that for P_M we

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can write with sufficient exactness, in place of Equation 37, the approximate expression

$$P_M = 1.15(2 - \alpha)P_S = \frac{115\Delta_B(2 - \alpha)}{\alpha C}. \qquad (38)$$

Combining this with Equation 31 and neglecting Δ_H we have

$$P_M = \frac{115(1 - \alpha)}{\alpha C}[H^+]_W. \qquad (39)$$

Substituting for $[H^+]_W$ from Equation 3 gives finally

$$P_M = \frac{1.15.10^5 \alpha L_W}{\Lambda_{H_2CO_3} K_E}, \qquad (40)$$

an expression from which one could calculate the metathesis correction for any uni-univalent salt of a strong acid and base dissolved in any conductivity water containing only carbon dioxide as an impurity. The expression is applicable for room temperatures, and values for K_E and α may be obtained from Table VII. The quantity P_M thus calculated represents the correction *in per cent.* which must be *added* to the ordinary "water corrected" value of the specific conductance (*i. e.*, to $L_S - L_W$) in order to obtain the *true specific conductance of the salt*, assuming all the time that CO_2 is the only impurity in the conductivity water. For example, for a 0.00005 N solution at 18° we have (Table VII) $K_E = 0.0210$, $\alpha = 1$, and $\Lambda_{H_2CO_3} = 353$. Substituting we find if $L_W = 1 \times 10^{-6}$, $P_M = 0.016\%$.

Before closing this discussion reference should be made to the work of previous investigators on this subject. For a fuller presentation and discussion of such work, together with a bibliography, the reader is referred to the papers by Kendall already mentioned.[1] The first important contribution to the subject, insofar as it concerns salts of strong acids and bases, was made by Arrhenius[2] about four years ago in connection with a general discussion of the "carbonic acid correction." Arrhenius computed the values of this correction for some dilute solutions of sodium chloride and sodium nitrate and obtained results and conclusions which directly contradict those of the writer. If the writer correctly interprets him, Arrhenius concludes that the "carbonic acid correction" for the salt of a strong acid and base (sodium chloride) dissolved in equilibrium water at 18°, is *negative in sign*, starting at zero for high dilutions, reaching a maximum of −0.1% at about 0.0001 N and then falling away to zero again at higher concentrations. This is a complete contradiction of the writer's conclusion that this correction should be *positive in sign* and should *increase continuously* with dilution reaching a maximum value of only +0.016% at high dilutions.

Kendall in his own discussion of this question apparently reaches the

[1] *Loc. cit.*, 39, 18.

[2] Arrhenius, *Medd. K. Vetenskapsakad. Nobelinst.*, 2, No. 42 (1913), especially p. 10.

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same conclusion that Arrhenius does[1], since he reproduces Arrhenius' calculations for sodium chloride as an illustrative example and states finally in his summary that the present "water corrected" values are slightly *too large*.[2] Neither Arrhenius nor Kendall gives any details of the calculations from which his conclusions were reached.

8. Influence of Saline Impurities upon the Metathesis Correction.—Let us assume in the following calculation that the conductivity of the "conductivity water" is due entirely to the presence of a strong electrolyte B′A′ whose equivalent conductance is Λ'. The products of metathesis will be the un-ionized molecules BA′ and B′A which, in the case under consideration, will be produced in equal amounts. The total concentration of the salt B′A′ will be $\frac{1000\,L_W}{\Lambda'}$.

The decrease Δ_I in the concentration of each ion species owing to metathesis will evidently be the same for all the four ions involved and will be practically equal to the number of equivalents of BA′ formed, which is given with sufficient accuracy by the following expression:

$$[BA'] = \Delta_I = \frac{\alpha C \times \alpha' C'}{K_E}. \tag{41}$$

The percentage decrease in the conductance due to the metathetical removal of the ions of each salt will therefore be

$$0.01 P_{BA} = \frac{\Lambda\,\Delta_I}{1000\,L_E} \tag{42}$$

or

$$P_{BA} = \frac{100\Lambda\alpha C\alpha' C'}{K_E \frac{C\Lambda}{1000} \times 1000} = \frac{100\alpha C'}{K_E} \tag{43}$$

for the ions for the salt BA; and similarly

$$P_{B'A'} = \frac{\Lambda'\alpha\alpha' C'}{K_E\,\Lambda} \tag{44}$$

for the ions of the salt B′A′.

Putting $C' = \frac{10^3 L_W}{\Lambda'}$ and adding, we find the total percentage metathesis correction to be

[1] Or else he accepts Arrhenius' conclusions without having given the subject any study himself. It is not entirely clear from his treatment of the subject just what is the real basis for his attitude on this point.

[2] His contradictory statement near the bottom of page 11 of the same paper is assumed by the writer to be unintentional and his true views on the subject are assumed to be those stated in the latter part of his paper which are in accord with those of Arrhenius.

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$$P'_M = \frac{10^5 L_W \alpha}{K_E}\left(\frac{1}{\Lambda'} + \frac{\alpha}{\Lambda}\right) \tag{45}$$

in which α has been written for α', and $\Lambda_C = \Lambda_0$ for both salts.

Curve C in Fig. 2. shows how P'_M varies with C in the case of potassium chloride, for $L_W = 10^{-6}$ and Λ' taken as 100. For this curve the abscissa scale represents *hundredths of a per cent.* instead of thousandths. By comparing Curves C and D it is evident that the metathesis correction due to a salt impurity in the conductivity water would be about *twenty times as large* as that due to a carbon dioxide impurity, for the same value of L_W.

In view of our lack of knowledge concerning the exact natures and amounts of the impurities present in the conductivity water employed by Kohlrausch, the following somewhat arbitrary method of correcting his data is proposed: From Curve D in Fig. 2 we find that the "carbon dioxide corrections" at 0.0001 N and 0.0002 N would be 0.015 and 0.016%, respectively. Since, however, the water employed by Kohlrausch contained some traces at least of basic or saline impurities (see below, Sec. 11), the true metathesis correction would be somewhat larger than the above figures. In lieu of any exact information, the writer proposes the round value 0.02% as the metathesis correction for these two concentrations, and the round value 0.01% for the concentrations 0.0005 N and 0.001 N, respectively, with no correction for higher concentrations. These corrections are at all events not too large and may be safely regarded as having all the accuracy that Kohlrausch's data themselves justify; in fact they are within the experimental error of Kohlrausch's measurements. The above corrections apply only to salts of strong acids and bases.

9. **Salts of Weak Acids and Bases.**—If the conductivities of solutions of sodium acetate could be studied at low concentrations (0.0001 N and below) with *absolutely pure water*, then in addition to a very appreciable "water correction" which would be *subtracted* in the usual manner, there would also be a comparatively large (*e. g.*, about 0.4% at 0.0001 N) metathesis correction which would have to be *added*. This metathesis correction would be the larger, the weaker the acid and it would be greatly increased by the presence of carbon dioxide in the water. In the case of absolutely pure water, however, practically no error would be involved in applying this correction since it could be accurately calculated, provided that the ionization constant of the acid were known with sufficient accuracy.

In the case of "equilibrium water," however, considerable uncertainty would be attached to the calculation of the metathesis correction owing: (1) to the magnitude of the correction; (2) to the uncertainty as to how much of the conductivity of the water could be ascribed to the carbonic acid; (3) to the uncertainty as to the natures of the other impurities and

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the metatheses which they would produce; and (4) to the already mentioned difficulty of maintaining a sufficient degree of constancy in the composition of equilibrium water under working conditions, owing to the variability of the atmosphere. For these reasons it seems to the writer that the only possible method for securing really dependable Λ_0 values in the case of salts of weak acids or bases (and consequently for determining the anion conductances of these weak acids and bases) is to employ "ultra-pure conductivity water" in making the measurements at high dilutions. Undoubtedly much more accurate conductance values than those at present accepted for salts of strong bases with weak acids can be obtained by applying a "carbonic acid correction" to the data now available,[1] but the weaker the acid involved, the greater will be the uncertainty attached to this procedure.

In the case of a salt of a weak base with a strong acid the presence of carbonic acid in the conductivity water tends to reduce the hydrolysis, and if the base is not too weak, a salt of this kind would behave very much like the salt of a strong acid and base. It is perhaps for this reason, for example, that the conductivity data given for thallous chloride and thallous nitrate appear to be substantially correct.

10. **Salts of Higher Valence Types.**—Owing to the presence of intermediate ions in solutions of salts of mixed valence types, such as K_2SO_4 and $MgCl_2$, the conductances of bi- and poly-valent ions are best obtained from the Λ_0 values for salts of unmixed valence types; for example, the conductance of magnesium ion could probably be most reliably calculated by determining the Λ_0 value for magnesium sulfate rather than from attempting to determine directly the Λ_0 value of magnesium chloride. In all cases the metathesis corrections for salts of the higher valence types are *very much larger*[2] than they are for uni-univalent salts and furthermore there would always exist some uncertainty in applying a "carbonic acid correction" to a salt such as $MgSO_4$, owing to the formation in unknown amounts of the un-ionized molecules $MgCO_3$, $Mg(HCO_3)_2$, H_2SO_4 and $Mg(HSO_4)_2$. The present Λ_0 values for all salts of higher valence types must therefore be regarded as of *very doubtful accuracy*.

11. **Acids and Alkalies.**—A very considerable degree of uncertainty exists at the present time regarding the values of the conductances of hydrogen ion and hydroxyl ion owing to the entire lack of accurate values for the true specific conductances of dilute solutions of acids and alkalies. It has been noticed by numerous investigators that the measured values of the equivalent conductances of strong acids reach a maximum at about 0.0001 to 0.0002 N thereafter decreasing again. This so-called "abnormal

[1] Cf. Kendall's recalculation of the data for NaF, THIS JOURNAL, 39, 22 (1917).

[2] For example, if $MgSO_4$ is 90% ionized at C = 0.0001 N, the "carbonic acid" correction for equilibrium water would be more than 0.3%, possibly as much as 0.5%, as compared with only 0.015% for a uni-univalent salt.

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behavior" is also exhibited even after a "carbonic acid correction" has been applied to the data, as Kendall discovered.[1]

Because of this behavior Kendall considers that "there must exist some general disturbing influence not yet taken into consideration," and he promises a more detailed discussion of this matter in a later paper. With this statement of Kendall's the writer finds himself in complete accord, with, however, the added conclusion[2] that the "general disturbing influence" referred to is the presence of basic or saline impurities, or both, in the conductivity water, in amounts which are far from being negligible. The influences of such impurities are much more apparent when studying solutions of acids than in the case of neutral salt solutions because metathesis is larger and results in the removal of the ion to which 80% or more of the conductance of the electrolyte is due. It seems, therefore, to the writer than the above so-called "abnormal behavior" of acids should be taken as conclusive proof that the whole of the conducting impurity in ordinary conductivity water cannot in general be regarded as carbonic acid and hence that any proposal to employ equilibrium water and to calculate "exact" metathesis corrections cannot be approved as a general and primary method for obtaining true specific conductances at high dilutions.[3]

URBANA, ILL.

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF ILLINOIS. PUBLICATION No. 30.]

THE EQUIVALENT CONDUCTANCE OF ELECTROLYTES IN DILUTE AQUEOUS SOLUTION.

II. THE EXTRAPOLATION OF CONDUCTIVITY DATA TO ZERO CONCENTRATION.

BY EDWARD W. WASHBURN.

Received September 25, 1917.

CONTENTS.—1. Introduction. 2. The Method of Kohlrausch. 3. The Method of A. A. Noyes. 4. The Equation of Kraus. 5. The Equation of Bates. 6. A New Graphical Method of Extrapolating. 7. Bates Method for Computing Λ_0.

1. Introduction.—In order to determine the value of Λ_0 and also the limiting value K_0 of the Mass-Action expression

[1] THIS JOURNAL, 39, 13 (1917). The "carbonic acid correction" in this instance was, within the experimental error of the data employed, equal to the water correction, which it, therefore, canceled.

[2] Frequently suggested in the past by various investigators.

[3] In footnote 1, page 13, of his second paper, Kendall makes the statement that "The concentrations of any other electrolytes present must be so minute that the conclusions obtained cannot, in any case, be significantly affected." It seems to the writer that such a statement fails to give sufficient weight to the fact that in many cases saline or alkaline impurities are much more effective than carbon dioxide. This is true even, for example, in the simple case of neutral salts as explained in Sec. 8 above. Cf. Kohlrausch and Holborn, *Leitvermögen*, p. 92.

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$$\frac{\alpha^2 C}{1 - \alpha} = K_E \tag{46}$$

when $C = 0$, it is necessary to extrapolate the observed conductance data from the lowest concentration measured. This extrapolation has been usually carried out in the past by fitting some empirical function to the observed values over at least the lower portion of the concentration range open to measurement and then employing this function expressed either graphically or in the form of an equation) for determining Λ_0, or both Λ_0 and K_0. A comparison of the values obtained from the different functions employed, as well as a comparison of the arguments advanced by the authors of these functions in support of the values deduced by them, brings out in a rather striking manner the general untrustworthiness of most of the methods heretofore employed.

2. **The Method of Kohlrausch.**—For determining the value of Λ_0, Kohlrausch employed the following two-parameter equation:[1]

$$\Lambda_0 = \Lambda_c P C^{1/2} \tag{47}$$

With regard to the validity of this method of extrapolation in the case of uni-univalent salts, Kohlrausch had the following to say:[2]

"In the case of these salts it seems to me that there can be no possible doubt as to the method which is at present the most probable one, because for these salts the above equation reproduces the experimental data between 0.0001 and a few thousandths N with practically complete agreement.....Since, therefore, the change of the conductivity with increasing dilution is reproduced with such exactness by such a simple relationship, it seems to me very probable that this relationship expresses a general law. This relationship admittedly does not agree with the conclusions that follow from the ionic theory which, indeed, leads to quite another relationship. This fact alone, however, cannot be considered as an objection to the relationship because there can no longer be any doubt that the consequences of the ionic theory are applicable only to weak electrolytes. The conductivity of strong electrolytes is determined by other phenomena in the solution, among which possibly polymerization is the most important. It is, of course, unfortunate that the theory does not take account of these relationships but this cannot at present be helped. At the present time I believe that the above *empirical relationship constitutes the only basis upon which extrapolation can be made.* I conclude, therefore, that this is the method which should be employed." (The italics are mine.)

By modifying the above function slightly so as to give the *three*-parameter equation

$$\Lambda_0 = A\Lambda_c + \Lambda_c^p C^{1/2} \tag{48}$$

Kohlrausch found (not unnaturally) that he was able to fit the new equation to the observations up to concentrations as high as 0.1 N. The Λ_0 value obtained from this new function was practically identical with that given by the first function and Kohlrausch expresses the opinion that by employing the second function we have a means of calculating Λ_0 values

[1] Kohlrausch, "*Gesammelte Abhandlungen.*" 2, 1127, 1131, 1132.

[2] *Loc. cit.*, pp. 1131, 1132.

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from the data for more concentrated solutions, thus avoiding entirely the necessity of measuring dilute solutions.[1]

3. The Method of A. A. Noyes.—The graphical method of extrapolation employed by A. A. Noyes and his associates[2] resembles Kohlrausch's method insofar as it involves the assumption that strong electrolytes do not obey the Mass-Action law even at high dilutions. In fact, as Bates has pointed out,[3] in this method the value of K_E is implicitly assumed to decrease without limit and to approach zero when C becomes zero.

Now the theoretical basis for the Mass-Action law is so sound that any method which denies the validity of this law as a limiting condition for *all* electrolytes must, it seems to the writer, be henceforth rejected on this ground alone, if for no other reason. Contrary to the above statement of Kohlrausch there has never been any real evidence presented which would require the conclusion that the ionization equilibrium of strong electrolytes follows a law which is inconsistent with the Mass-Action law at high dilutions. Of course it is true[4] that if one starts with the *a priori* assumption that the Mass-Action law will never be obeyed and then proceeds to derive a Λ_o value in harmony with this assumption then naturally it might not be difficult with the aid of this Λ_o to compute values for the Mass-Action expression K_E, which would not exhibit any pronounced tendency to conform to the Mass-Action law, but such a behavior should scarcely be considered as evidence in support of such a view as that of Kohlrausch, quoted above.

4. The Equation of Kraus.—A four-parameter empirical equation of the form

$$\frac{\Lambda_c^2 C}{\Lambda_o(\Lambda_o - \Lambda_c)} = K_E = K_o + k\left(C\frac{\Lambda_c}{\Lambda_o}\right)^h \qquad (49)$$

where Λ_C is the "corrected" (*i. e.*, for viscosity) equivalent conductance, has been proposed by Kraus as a general relation for expressing the dependence of conductance upon concentration. In a careful and exhaustive study of all the conductivity data available in the literature, Kraus and Bray[5] have shown that this equation, with but few exceptions, is generally applicable to all such data. An important exception occurs in the case of aqueous solutions of strong electrolytes. Using the data of Kohlrausch and Maltby for potassium chloride, Kraus and Bray state that

"With the exception of the point at 3 normal the calculated values check the experimental values within 0.1% which is the limit of the experimental error.[6] Beyond

[1] Cf. the similar reasoning of Kraus and Bray referred to below in footnote 3, p. 126.

[2] See Noyes and Falk, THIS JOURNAL, **34**, 462 (1912).

[3] THIS JOURNAL, **35**, 522 (1913).

[4] As Wegscheider has pointed out (*Z. physik. Chem.*, **69**, 621 (1909)).

[5] THIS JOURNAL, **35**, 1315 (1915).

[6] This statement is not strictly correct as the data of Kohlrausch and Maltby are considerably more accurate than 0.1%.

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0.001 N the conductances calculated by means of the equation are smaller than those determined experimentally by Kohlrausch and Maltby."

Because of the failure of their equation to fit the observed data in the lower portion of the concentration range, Kraus and Bray question the validity of these data. The Λ_0 value 128.3 which they obtain by disregarding these data is consequently quite different from that, 130.0, obtained by the Kohlrausch method from the same experimental data. As arguments in favor of the validity of their conclusions, Kraus and Bray make the following statements:[1]

"There is always a possibility that the discrepancy in these dilute solutions is due to experimental error, such as uncertainties in the correction for the conductance of the solvent. An increase of 10% in the correction for the solvent would bring the conductances between 0.001 N and 0.0001 N into agreement with Equation 3. It should be borne in mind that in these dilute solutions we have a highly complex equilibrium between the solute, the solvent and its ions, and an unknown constituent which, in part, probably consists of carbonic acid. Taking all these factors into account, it may well be expected that the corrections made for the solvent are in error by as much as 10%. It certainly would be an unjustifiable procedure to assume, after showing that a certain dilution law holds true from 3 normal to 0.001 normal within the limits of experimental error. that the law suddenly undergoes an enormous change after reaching a dilution where there is good reason, from a theoretical standpoint, for believing that the law must hold.

"It should not be forgotten that the general equation has been found to apply to an enormous number of solutions over extreme ranges of concentration in other solvents than water, including the alcohols, which are closely related to water. Moreover, this equation admits of a rational theoretical interpretation in dilute solutions. Further, many electrolytes in water, namely, the organic acids and bases, and mercuric chloride, a weakly dissociated salt, all obey the Mass-Action law in water. To cast aside all this mass of positive evidence because of results obtained for strong electrolytes in water at concentrations below 0.001 N would be an irrational procedure."

Except for the important difference that the Kraus equation reduces to the Mass-Action law at high dilutions, there is a striking similarity between the method of reasoning followed by Kraus and Bray and that followed by Kohlrausch. In both instances the fact that the equation fits the data over the concentration range involved is taken as evidence supporting the conclusion that the extrapolated value of Λ_0 to which it leads must be the correct one. It seems to the writer however that the course of reasoning followed by Kraus and Bray must be condemned as illogical at almost every point, for the following reasons:

In the *first* place, their calculated conductance values below 0.001 N are *lower* than the observed values, a fact which they ascribe to "a highly complex equilibrium between the solute, the solvent and its ions, and an unknown constituent, which in part, probably consists of carbonic acid." Now as explained in the first paper of this series, any metatheses which could possibly take place between the salt ions and *any other ions* which

[1] THIS JOURNAL, 35, 1413 (1915).

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might be present in the conductivity water would *always and necessarily* result in making the ordinary "water corrected" values for the salt conductivity *too small*, instead of too large, and whatever might be the magnitude of this error the *true conductance values* must necessarily be *larger* than those given by Kohlrausch and Maltby, and must therefore be *even farther away* from the "*calculated values*" obtained by Kraus and Bray. In other words no possible error in the "water correction" could account for the discrepancy between the observed values and those calculated from the Kraus equation.[1]

Secondly, the fact that their equation holds fairly well within the concentration range, 3 N to 0.001 N, is, it seems to the writer, no reason at all, as they assume (and as Kohlrausch similarly assumed for his function) for concluding that it must hold below 0.001 N. There must indeed be a great many functions[2] which could be fitted to any desired portion of the *actual* conductivity curve with any desired degree of exactness but which would deviate from the course of this curve in other portions and which would yield a great variety of different Λ_0 and K_0 values.[3]

Thirdly, the assumption made by Kraus and Bray that there is good reason from a *theoretical standpoint* for believing that their equation must hold at high dilutions is also wholly unsupported by any evidence and, in the opinion of the writer, is entirely without justification, as will be explained further below.

5. The Equation of Bates.—In endeavoring to find, for interpolation purposes, a function which would satisfactorily express the relation between conductivity and concentration, Bates discovered that the following mathematical form was capable of expressing the conductivity data of Kohlrausch and Maltby for potassium chloride between the concentrations 1.0 N and 0.0001 N with great exactness, much more accurately in fact than was the case with the equation of Kraus.[4]

[1] Unless indeed one wished to advance a purely *ad hoc* hypothesis to the effect that the conducting power of the carbonic acid is considerably increased by the simple presence of the salt in the solution, an hypothesis contrary to the accepted facts concerning the influence of small amounts of strong electrolytes upon the ionization of weak ones.

[2] Cf. Wegscheider, *Loc. cit.*, p. 622.

[3] The error in logic involved in an argument of this kind is a very common one and has been made in the past by many investigators (the writer among others). It seems, therefore, necessary to emphasize the fact that in general, values obtained by extrapolation from a purely empirical equation carry no assurance whatever of being correct, the uncertainty being the greater the longer the extrapolation involved and the larger the number of parameters required in the empirical equation employed. In the remark by Kraus and Bray, that, "For a more accurate determination of Λ_0, accurate conductance and viscosity data should be available *between 1 and 5 normal*," (*Loc. cit.*, p. 1412, footnote 3. The italics are mine), the above fallacious argument seems to the writer to have attained its height of absurdity.

[4] See Washburn. "Principles of Physical Chemistry," 1915, p. 215, McGraw-Hill Book Co., N. Y.

The Bates equation is a three-parameter equation since the value of Λ_0 employed

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$$\log \frac{\Lambda_c^2 C}{\Lambda_0(\Lambda_0 - \Lambda_c)} = \log K_E = \log K_0' + k'\left(C\frac{\Lambda_c}{\Lambda_0}\right)^{h'} \qquad (50)$$

In other words, if the above arguments advanced by Kraus and Bray in support of their equation and the value of Λ_0 to which it leads had any validity whatever, these arguments would all apply with much greater force to Bates' equation which employs a decidedly different value of Λ_0. A comparison of the accuracies with which the three functions of Kohlrausch, of Kraus, and of Bates, respectively, are capable of expressing the experimental data is shown in Fig. 3.

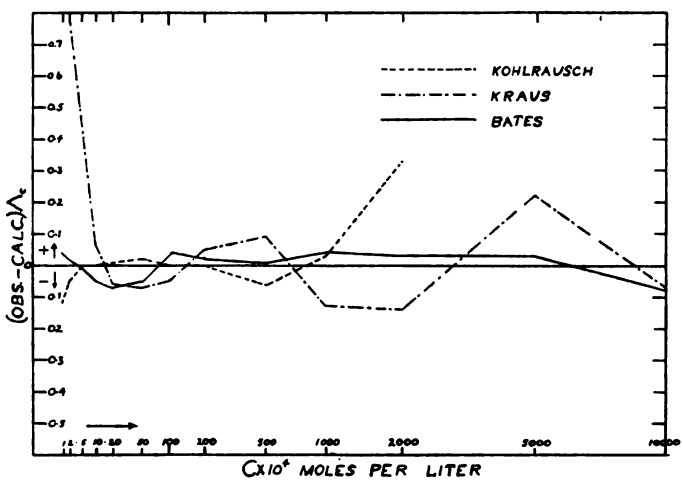

Fig. 3.—Illustrating the difference between the observed and calculated equivalent conductances of potassium chloride solutions using the empirical functions of Kohlrausch, Kraus, and Bates, respectively. The ordinates represent units of equivalent conductance.

Because the equation of Bates fits the experimental data *down to the lowest concentrations heretofore measured*, and with such a high degree of accuracy, most of the arguments employed by Kraus and Bray would lead to the conclusion that Bates' equation therefore represents the correct law connecting concentration and conductivity between zero and 1.0 N and that hence the value of K_0' in the Bates equation represents the true value of the limit approached by the Mass-Action expression as C approaches zero. Such a conclusion as this, however, would be wholly unjustified. The values (0.08 and 0.0039, respectively) of K_0 and K_0' in the Kraus and in the Bates equations, respectively, which on the basis of

is not obtained by extrapolating the function itself but is obtained quite independently by an entirely different method which will be referred to below. Furthermore, Bates correctly regards his equation merely as an empirical interpolation equation for the concentration range in which it applies and does not ascribe any theoretical significance to any of its parameters.

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the above point of view represent the same quantity, are evidently very far from being identical and in the writer's opinion there would be no justification whatever for concluding that either one of them represents the correct value of the limit of K_E when $C = 0$.

It will be noted that the forms of both the Kraus and the Bates equations fulfill the condition of obedience to the Mass-Action law when $C = 0$, and because of this fact Kraus and Bray seem inclined to attach to their own equation some theoretical significance. The mere fact that the Bates equation would, from such a standpoint, have an equally good theoretical basis is alone sufficient to destroy the force of their reasoning. Each equation imposes upon the electrolyte an *arbitrary method of approach* to the condition of constancy required by the Mass-Action law at high dilutions. The two methods of approach are both radically different and naturally both wrong since there is no reason whatever for supposing that either function represents the data between $C = 0$ and C equals the lowest concentration measured. In fact, any method of extrapolation which imposes *an arbitrary a priori determined* path over which the values of K_E shall approach constancy must obviously be rejected if we are to expect to obtain from it reliable values for Λ_0 and K_0.

6. A New Graphical Method of Extrapolating.—In order to avoid the errors involved in what may be called the "arbitrary function" methods of extrapolating, and also to avoid the similar uncertainties involved in attempting a direct graphical extrapolation, the following method has been devised: It seems to the writer that no valid objection[1] can be urged against it. It rests only upon the following two assumptions: (1) That as C decreases, the value of the Mass Action expression K_E also decreases and will eventually gradually approach a constant, K_0, at extreme dilutions; and (2) That whatever be the true form of the curve connecting K_E with C it must be one which does not show deviations from the Mass-Action law which *increase with dilution*, that is, in dilute solutions the curve must not exhibit any erratic behavior such as a sudden rise or a

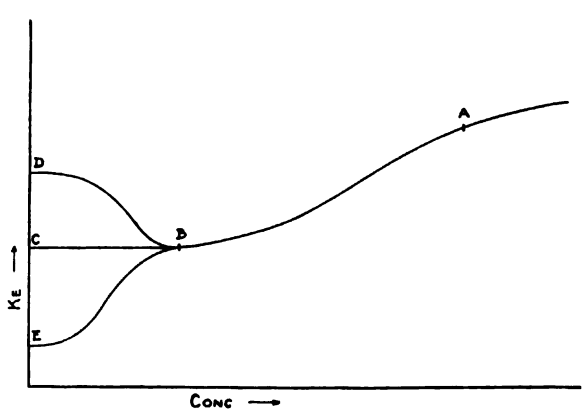

Fig. 4.

[1] Unless indeed the assumption that, $\lim_{C=0} dK_E/d_{C=0}$, is considered an objection.

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sudden fall with decreasing concentration. For example, if the values of K_E are found to follow the path AB (Fig. 4) to some low concentration B, it is assumed that they cannot thereafter describe such a path as BD or BE, but must instead follow the path BC.

In other words, it is assumed that those influences which cause a strong electrolyte to deviate from the Mass-Action law at high concentrations *gradually and steadily* become smaller and smaller and finally disappear at infinite dilution. No assumption is made as to an actual path over which the values of K_E shall approach the constant limiting value, nor in fact is any assumption whatever made as to the mathematical form of the function which connects the conductivity with the concentration *over any part of the concentration range* open to direct measurement.

The new method consists simply in plotting values of K_E, the Mass-Action expression, against corresponding values of the concentration, employing different assumed values of Λ_0 and rejecting those values which cause the curve in dilute solutions to exhibit radical changes in direction.

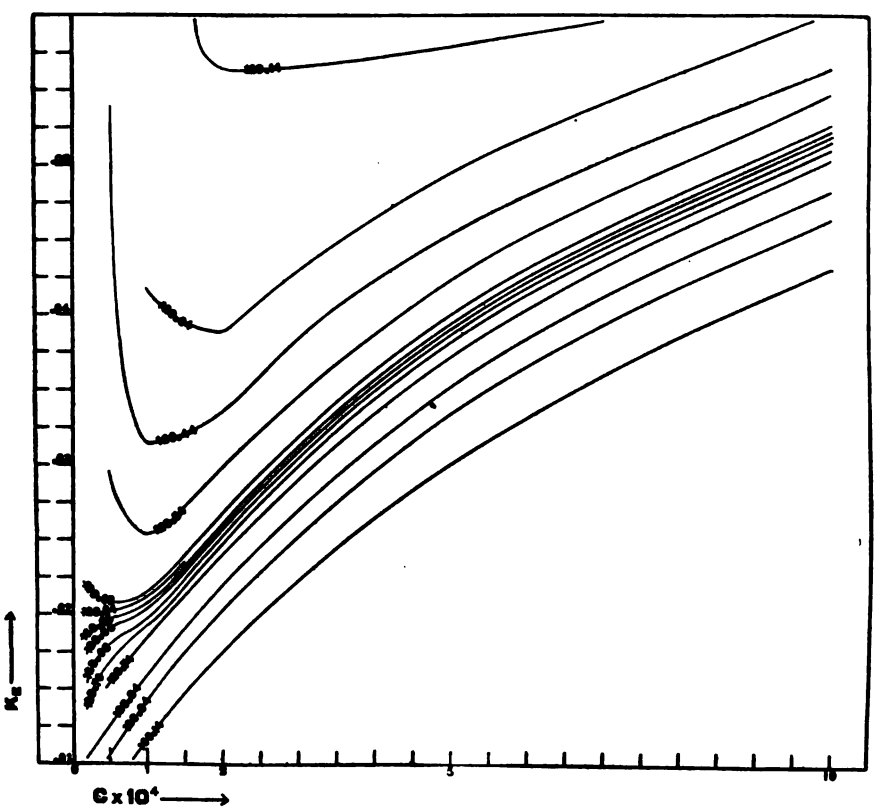

Fig. 5.—Illustrating a new method for determining Λ_0.

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In this way one finds that, if the value of Λ_0 employed be too small, the curve will eventually shoot upward in the lower concentration ranges, while if the Λ_0 value employed be too large the curve will turn downward in the lower concentration ranges. By employing this method it is possible to determine the value of Λ_0 with a precision of 0.01%, provided the conductance data themselves are as accurate as this and extend at least as low as $C = 00002\ N$. This will become evident from an inspection of Fig. 5 which has been constructed from the conductance values obtained by Kohlrausch and Maltby and by Weiland, and which are tabulated in Table VII, page 146. For conductance data which only go as far as 0.0001 N this method enables one to determine the Λ_0 value to about 0.2%.

7. **Bates' Method for Computing Λ_0.**—The best method heretofore suggested for determining Λ_0 values is that devised by Bates.[1] This method is in a way an "arbitrary function" method since it employs the Storch equation, but as a matter of fact the uncertainties characteristic of "arbitrary function" methods in general happen to be largely eliminated in this particular method because in the process of applying the "arbitrary function" to the conductance curve it is only fitted to a small piece of the curve at a time, with the result that its two parameters, which are allowed to vary in different portions of the curve, are sufficient to secure a fairly accurate fit. There must also obviously be other functions than the Storch equation, which if carefully handled in this way could be similarly made to give reliable Λ_0 values.

In Bates' method the Storch equation

$$\frac{\Lambda_c^n C^{n-1}}{\Lambda_0^{n-1}(\Lambda_0 - \Lambda_c)} = const. \qquad (51)$$

is employed to determine an upper and a lower limit, respectively, for Λ_0. The lower limit is obtained by putting $n = 2$, and solving for Λ_0, using the Λ_c values for the two lowest concentrations measured. In other words, the Mass-Action law is assumed to hold between these two lowest concentrations.

The upper limit for Λ_0 is determined by finding by trial the largest value which can be employed for Λ_0 without causing the corresponding values of the exponent n to pass through a maximum. In other words, assuming that the Storch equation correctly expresses the conductivity curve between each pair of concentrations (an arbitrary assumption, which is of course not exactly true, but very nearly so, as explained above), then the value of n is so chosen that the magnitude of the deviation of the electrolyte from the Mass-Action law (which deviation is indicated by the magnitude of the exponent $2-n$) shall be a minimum between the two lowest concentrations measured.

[1] THIS JOURNAL, 35, 527 (1913).

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Except for the assumption of a definite form of function, the Storch equation, the method of Bates rests upon substantially the same character of a foundation as the one proposed by the writer, being in fact an analytical method for attaining the end which the writer secures by a graphical process. As a matter of fact when both methods are applied to the data for potassium chloride they give very nearly the same result for Λ_0. The Λ_0 values given by Bates' method are on the average only about 0.05 unit lower than those obtained by the writer's method, as shown in Table VI.

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF ILLINOIS. PUBLICATION NO. 31.]

THE EQUIVALENT CONDUCTANCE OF ELECTROLYTES IN DILUTE AQUEOUS SOLUTION.

III. A STUDY OF DILUTE SOLUTIONS OF POTASSIUM CHLORIDE.[1]

BY HENRY J. WEILAND.[1]

Received September 25, 1917.

CONTENTS.—1. The Preparation of Ultra-Pure Conductivity Water. (*a*) The Work of Previous Investigators. (*b*) Outline of the Distillation Process Employed in This Investigation. 2. Description of Apparatus and Experimental Procedure. (*a*) Description of Apparatus. (*b*) Collecting the Ultra-Pure Conductivity Water. 3. The Conductivity of Dilute Solutions of Potassium Chloride. (*a*) Preparation of the Solutions. (*b*) Densities of the Solutions. (*c*) Determination of the Cell Constant. (*d*) The Conductivity Data. 4. The Adsorption of Potassium Chloride by Quartz. (*a*) The Adsorption Correction and Method of Determining It. (*b*) Preparation of the Quartz Fragments. (*c*) Determination of the Surface of the Quartz. (*d*) Experimental Procedure and Results. (*e*) Calculation of the Adsorption Correction. 5. Discussion of the Results of the Investigation. (*a*) The Experimental Error. (*b*) Consistency of the Data. (*c*) Calculation of Λ_0 and of K_0. (*d*) Conductance Values at Round Concentrations. (*e*) Potassium Chloride and the Law of Mass Action. (*f*) The Interpolation Equations of Kraus and of Bates. 6. Summary.

1. The Preparation of Ultra-Pure Conductivity Water.

(*a*) **The Work of Previous Investigators.**—The purest water ever obtained was that prepared by Kohlrausch and Heydweiller in 1894. Their process consisted in the repeated back-and-forth distillation of water between two evacuated glass vessels, one of which was provided with electrodes. After 42 distillations of this kind Kohlrausch and Heydweiller obtained water with a minimum conductance of 0.043×10^{-6} reciprocal ohms at 18°. The quantity of water prepared in this way was but a few cubic centimeters, not a sufficient quantity to be used in measuring the conductivity of solutions of electrolytes.

The attempts of later investigators in this field have been directed toward the problem of preparing conductivity water for use in making up

[1] Based upon a thesis submitted to the Graduate School of the University of Illinois, by the author, in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry, June, 1917.

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and measuring the conductivity of solutions, and since a review of the investigations upon this subject has recently been published by Kendall[1] further discussion of the subject will be omitted here. For the sake of completeness, however, mention may be made of the fact that in addition to the examples, cited by Kendall, of very pure conductivity water obtainable by distillation in contact with the atmosphere, investigators in this laboratory[2] have at times obtained water, by a single distillation of ordinary laboratory "distilled water," which had an initial and transitory specific conductance as low as 0.15×10^{-6} at 25°.

(*b*) **Outline of the Distillation Process Employed in This Investigation.**—The process employed for obtaining the ultra-pure conductivity water required for this investigation consisted in heating about 13 liters of good conductivity water (0.6 to 0.8 water) in a quartz still (Fig. 6) and at the

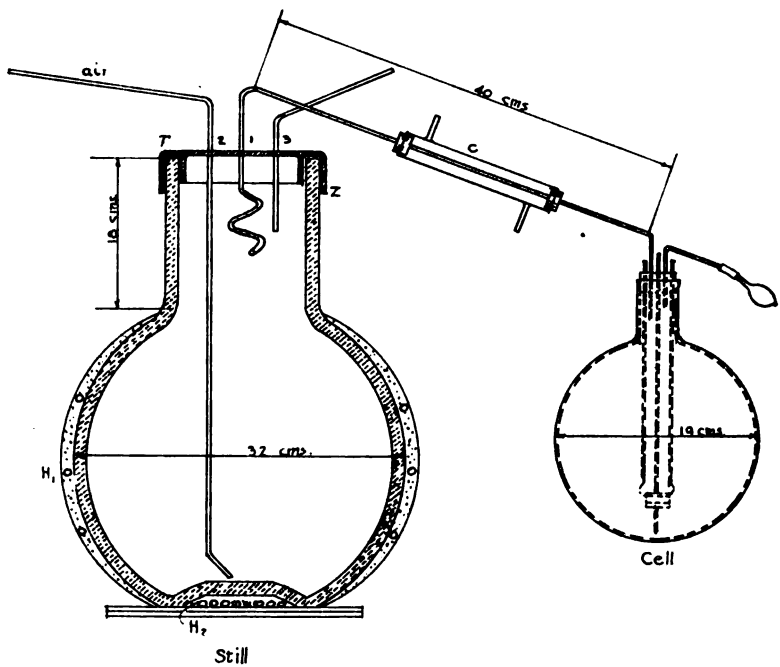

Fig. 6.—The distillation apparatus and conductivity cell.

same time passing a stream of carefully purified air through the water, which was maintained at a temperature a few degrees below its boiling point. This process[3] sweeps out of the water practically all of the dissolved gases which it contains without carrying over by entrainment any

[1] THIS JOURNAL, 38, 2460 (1916).

[2] See Bell, Univ. of Ill., *Thesis*, 1913, p. 15.

[3] The same principle is applied in a different way in the apparatus of Bourdillon, *J. Chem. Soc.*, 103, 791 (1913).

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particles of the liquid itself. This sweeping out process was continued for about 20 hours, after which a conductivity cell (Fig. 7), consisting of a three-liter quartz flask fitted with sealed-in platinum electrodes,[1] was

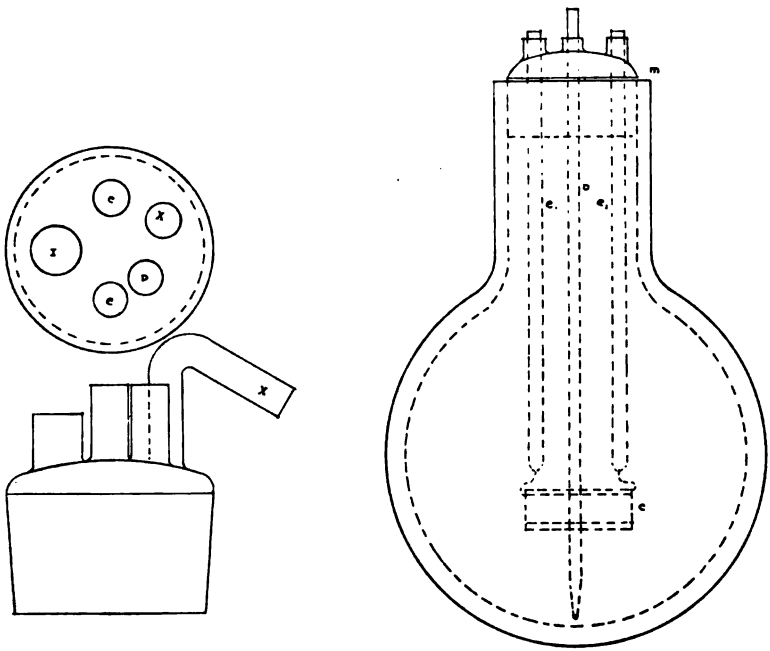

Fig. 7.—The conductivity cell.

attached to the block tin condenser of the above still and a distillate of about two liters was collected. If this distillate was found to be not sufficiently pure, it was drawn out of the cell by means of a quartz tube provided for that purpose and a second distillate was collected in the same way. This process of collection and rejection was then continued until finally about three liters of water having a specific conductance between 0.05 and 0.07 $\times$ 10^{-6} reciprocal ohms was obtained.

Since as explained in Sec. 2 of the first paper of this series nothing would be gained by employing water of a higher degree of purity than this, no attempt was made to prepare such water in connection with this investigation. The apparatus devised for this investigation could, however, readily be adapted to a repetition of the work of Kohlrausch and Heydweiller for the purpose of ascertaining what the conductivity of the purest water is.

[1] Thanks are due to Drs. R. D. Mailey and F. G. Keyes of the Cooper Hewitt Company for their valued assistance in making this difficult and important seal for us and thus placing at our disposal a pair of electrodes which have proved entirely satisfactory in every respect.

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2. Description of Apparatus and Experimental Procedure.

(*a*) **Description of Apparatus.**—In order to save space a detailed description of the apparatus and experimental methods will be omitted here, since this description is given in the author's thesis.[1] It will suffice to say that all necessary precautions were taken to insure the highest attainable degree of accuracy in the measurements. The conductivity water and the solutions were kept under pure air purified by means of the apparatus shown in Fig. 8. The measurements were carried out in an

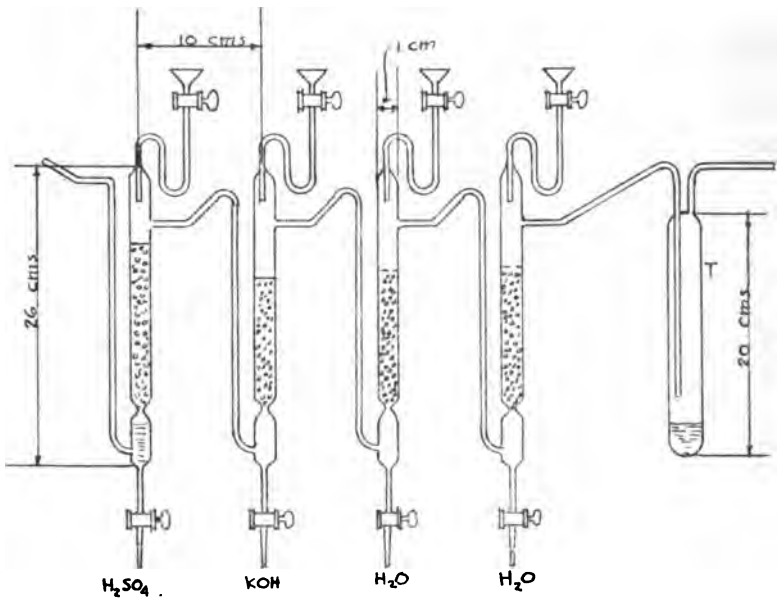

Fig. 8.—The air purification apparatus.

oil thermostat maintained constant to 0.01° and the electrical measurements were made with the apparatus described by Washburn and Parker[1] and are referred to resistance standards certified by the National Bureau of Standards. Previous to each set of measurements the electrodes were thoroughly cleaned by steaming them in the apparatus shown in Fig. 9. The solutions were made up in the conductivity cell by adding small individual crystals of the salt weighed on an assay balance and the solution was stirred constantly by a stream of purified air previously saturated and brought to the temperature of the bath.

(*b*) **Collecting the Ultra-Pure Conductivity Water.**—By the procedure described in Sec. 1, it was always possible with one filling of the large quartz still to obtain at least three liters of ultra-pure conductivity

[1] For copies of this thesis application should be made to the Librarian of the University of Illinois, Urbana, Ill.

[1] THIS JOURNAL, 38, 2431 (1916); 39, 235 (1917) and a paper not yet published.

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water. The quality of the water obtained in seven distillations is shown in Table II.

TABLE II.

Specific Conductance of Ultra-pure Conductivity Water Prepared on Different Dates. Temp. 18°.

Date.	12/28/'15.	1/15/'16.	3/18/'16.	2/2/'17.	2/19/'17.	2/24/'17.	3/6/'17.
$L_w \times 10^6$.	0.057	0.059	0.062	0.066	0.061	0.063	0.053

Water of this degree of purity can be kept in the quartz cell practically unchanged for periods as long as 12 hours, provided the stream of purified air is kept slowly bubbling through it. Some experiments were made to determine whether any pollution of the water was caused by withdrawing the stopper from opening 1 (Fig. 7) for 30 seconds and then replacing it. No change in the conductivity of the water could be detected under these circumstances. In making a series of conductance measurements of dilute solutions the length of time required is from two to three hours. The above experiments show that there is no danger of the water becoming appreciably contaminated during the time required for such a series of measurements.

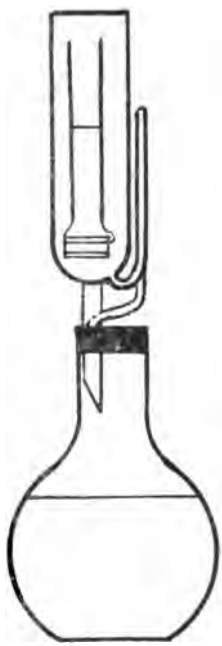

Fig. 9.—Apparatus for cleaning the electrodes.

3. The Conductivity of Dilute Solutions of Potassium Chloride.

(*a*) **Preparation of the Solutions.**—The potassium chloride employed in this investigation was Kahlbaum's special "K" product which was recrystallized three times from conductivity water, dried with the aid of a centrifuge and finally fused in platinum. It was kept for use in small weighing bottles over calcium chloride in a desiccator.

The solutions were made up by dropping successive small crystals into the cell. The crystals were weighed out on the small platinum balance pan and then transferred carefully to a shallow platinum bucket made from platinum foil. The salt crystals and the bucket were then dropped together into the conductivity cell. Blank experiments using the platinum alone demonstrated that no contamination of the water occurred during this operation.

It had been the original intention to use a microbalance for weighing the salt crystals but the balance provided for this purpose was not in shape for use at the time the final experiments were started and since there was not sufficient time to have it repaired recourse was had to a good assay

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balance which had a sensitivity of 0.001 mg. with a load of 20 mg. The weights employed had been calibrated at the U. S. Bureau of Standards. At the end of a series of measurements the conductivity cell and its contents were removed from the bath and weighed. The contents of the cell were then poured out and, after cleaning and drying, the cell and electrodes were again weighed thus giving the total weight of the final solution measured, which together with the weights of the different portions of salt added gave the necessary data for calculating the concentrations of the series of solutions. All the weighings were reduced to *vacuo*.

(*b*) **Densities of the Solutions.**—The densities employed in computing the concentrations of the solutions were calculated from the data of Lamb and Lee[1] by means of the following equation which is based upon their data:

$$D_{18°/4°} = 0.998622 + 485 \times 10^{-4}\, C \qquad (52)$$

(*c*) **Determination of the Cell Constant.**—The conductance values given in this paper are based upon the assumption that a solution of potassium chloride containing 7.43000 g. of salt in 1000 g. of solution (weights in air) has a specific conductance of 0.01288 reciprocal ohm at 25° and a specific conductance of 0.00715 reciprocal ohm at 0°. The cell constant was determined as follows:

The constant of a conductivity cell of type B[2] was first determined by measuring its resistance when filled with the above 0.1 *N* solution of potassium chloride at 25°. The value of its constant was found to be 0.6043 which checked to 0.02% a determination previously made by Clark who employed this same cell in 1915. Clark found the value 0.6044 at 25° and 0.6030 at 0°, giving for 18° the value 0.6040. After having determined the cell constant of this auxiliary cell in this manner, a comparison solution, approximately 0.001 *N* with respect to potassium chloride, was made up using conductivity water with a specific conductance of about 0.8×10^{-6} reciprocal ohms. The resistance of this comparison solutions was then measured in the auxiliary cell and also in the quartz cell employed in this investigation, and in this way the cell constant of the latter cell could be calculated. The results are shown in the following table:

Date.	Resistance in quartz cell.	Resistance in comparison cell.	Cell constant of quartz cell.
Feb. 26.....	146.443	3631.62	0.024356
March 6.....	134.366	3333.23	0.024348
March 16.....	118.222	2932.22	0.024352
		Value adopted,	**0.024354**

In addition to the above determination of the cell constant, an additional check was obtained in three of the runs by adding sufficient salt to bring

[1] Lamb and Lee, THIS JOURNAL, 35, 1687 (1913).

[2] Washburn, *Ibid.*, 38, 2449 (1916).

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the final concentration of the solution up to about 0.001 N, at which concentration a comparison with the conductance data of Kohlrausch and Maltby could be directly made. This comparison is shown in Curve A of Fig. 10, the concentrations being indicated at the top of this diagram

TABLE III.

Values of the Specific Conductance and Equivalent Conductance of Potassium Chloride Obtained in the Different Series of Experiments. Temperature, 18 ± 0.01°. Equivalent Weight of Potassium Chloride = 74.560. All Weights Reduced to *vacuo*.

$C \times 10^6$. (Micromols per liter.)	$L \times 10^6 = (L_s - L_w) \times 10^6$. ("Water corrected.")	Λ_C. Equivalent conductance.
Jan. 24, 1917.	$L_w = 0.07404 \times 10^{-6}$.	
23.958	3.10226	129.49_0
46.129	5.96758	129.36_8
81.343	10.5047	129.14_1
119.574	15.4176	128.93_8
183.019	23.5580	128.72_0
Feb. 2, 1917.	$L_w = 0.06645 \times 10^{-6}$.	
7.4945	0.96881	129.26_8
26.467	3.42878	129.54_7
42.251	5.46522	129.35_1
74.563	9.62983	129.14_9
102.58	13.2337	129.00_5
Feb. 10, 1917.	$L_w = 0.06998 \times 10^{-6}$.	
23.821	3.08509	129.51_3
58.647	7.58402	129.31_5
103.837	13.4033	129.08_0
1021.87	130.007	127.22_4
Feb. 24, 1917.	$L_w = 0.06330 \times 10^{-6}$.	
31.951	4.13537	129.43_0
61.994	8.00763	129.16_6
123.36	15.9024	128.91_1
958.22	121.993	127.31_2
Mar. 6, 1917.	$L_w = 0.05335 \times 10^{-6}$.	
26.960	3.48776	129.36_9
60.878	7.86092	129.12_5
104.17	13.4308	128.92_6
154.14	19.8425	128.73_3
236.09	30.3397	128.51_0
1299.02	1648.06	126.86_9

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and the values of Λ_c at the right. From the above data it is evident that the cell constant is known with a precision of about 0.02 per cent.

(*d*) **The Conductivity Data.**—Five separate series of experiments were made with potassium chloride, the results obtained being shown in Table III. The specific conductance values shown are the ordinary "water corrected" values; that is, they are the measured specific conductances diminished by the conductance of the water in each case. A calculation of the metathesis correction on the assumption that the only impurity present in the water was carbon dioxide was made with the aid of Equations 8 and 30 to 34 inclusive, as described in the first paper of this series. The results showed that for the most dilute solution measured this metathesis correction amounted to only 0.0018% and was accordingly negligible. It would also be negligible even if a substantial amount of the residual impurity were a neutral salt.

4. The Adsorption of Potassium Chloride by Quartz.

(*a*) **The Adsorption Correction and Method of Determining It.**—In calculating the concentrations of these very dilute solutions of potassium chloride it is necessary to know whether or not an appreciable adsorption of the salt takes place on the quartz walls of the conductivity cell. Briggs[1] who studied the adsorption of hydroxides and carbonates of several metals by quartz found an appreciable adsorption. In the case of the chlorides of potassium, sodium and ammonium, however, he did not succeed in detecting any appreciable adsorption. Kohlrausch[2] also studied the possibility of an adsorption of neutral salts by the electrodes and concluded that no appreciable error from this source was to be feared.

In order to determine the magnitude of the adsorption coefficient of potassium chloride by quartz, the following method was employed: The specific conductance of a dilute solution of potassium chloride was first measured in a special cell arranged for the purpose and then a definite quantity of well cleaned quartz fragments were dropped into the solution and the specific conductance again determined. Knowing the change in conductance and the total quartz surface involved, the adsorption coefficient could be calculated.

(*b*) **Preparation of the Quartz Fragments.**—The quartz fragments employed in this study were prepared from pieces of broken quartz apparatus. The fragments were first broken up into small pieces and then ground in a ball mill. The resulting quartz powder was then washed thoroughly until a good grade of conductivity water showed no increase in conductivity after being stirred with the quartz fragments. The quartz fragments were then dried in a quartz flask, being heated to 300° C. to drive out the last traces of water.

[1] Briggs, *J. Phys. Chem.*, 9, 624.

[2] Kohlrausch, *Ges. Abhandl.*, 2, 381.

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(*c*) **Determination of the Surface of the Quartz.**—The surface of one gram of the quartz fragments was determined as follows: The entire amount of quartz was first separated into fractions by means of a set of standard sieves. The weight of each fraction was determined and the average diameter of the particles of each fraction was measured by means of a micrometer microscope. In calculating the surface of the particles they were assumed to be perfect spheres. The calculated surface was therefore much less than the true surface because the particles of quartz were of very irregular shapes. The surface of each fraction was calculated from the average diameter of the particle, the weight of the fraction, and the specific gravity of the quartz. The composition of the quartz thus determined is shown in Table IV*a*, from which we find that the total surface of the quartz was about 347 sq. cm per g., this value being, for the reasons stated, a lower limit.

TABLE IV*a*.

Sieve, meshes per inch.	Average diameter in mm.	Total surface of fraction. Sq. cms. 10^{-3}.	Weight of fraction in g.
40	0.282	0.120	1.25
60	0.246	0.678	6.15
80	0.149	2.405	13.20
100	0.0968	2.425	8.65
120	0.0721	1.200	3.19
200	0.0583	3.029	6.51
over 200	0.0320	7.037	8.29
Total,		16.89	47.24

(*d*) **Experimental Procedure and Results.**—The conductivity cell employed in the adsorption studies consisted of a 250 cc. quartz flask and a pair of plunge electrodes. The cell was first filled with "equilibrium water" and allowed to come to the temperature of the bath. After determining the specific conductance of the water a small weighed crystal of potassium chloride was dropped into the water and the specific conductance of the resulting solution determined. When the conductivity had become constant a weighed amount of clean quartz was then dropped into the solution and after stirring, the conductivity was again measured.

In order to determine the "polluting effect" of the quartz an equal weight of quartz was then added to the conductivity water alone and the increase in conductance of the water noted. This same increase was assumed to take place when the quartz was added to the solution and after making a correction for this "polluting effect" the remainder of the observed change in the conductance of the solution was ascribed to adsorption. The data for two experiments of this character are shown in Table IV*b*.

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TABLE IV*b*.

Calculation of the Adsorption Coefficient for Potassium Chloride on Quartz.

$$x = \frac{10^8 \Delta L_{Ad}}{129.5\, S} \text{ equivalents per liter per sq. cm.}$$

	Specific conductance, $L \times 10^9$.		Specific conductance, $L \times 10^9$.	
	Water.	Solution.	Water.	Solution.
After adding quartz	1.05483	105.770	1.0394	144.095
Before adding quartz	0.93033	105.748	0.9458	144.066
ΔL	0.124	0.022	0.0936	0.029
ΔL^s	0.022		0.029	
ΔL_{Ad}	0.102		0.065	
Surface of quartz, S	17350 sq. cm.		16650 sq. cm.	
Volume of solution, V	0.217 *l.*		0.235 *l.*	
Adsorption coefficient, x	9.9×10^{-12}		7.1×10^{-12}	
Conc. of soln., C	0.00083		0.00112	
Final values	$C = 0.001n$ $x = 8.8 \times 10^{-12}$			

(*e*) **Calculation of the Adsorption Correction.**—The inner surface of the three-liter quartz flask employed as the conductivity cell throughout this investigation was calculated from the diameter of the flask to be 1030 sq. cm. The actual surface was somewhat greater than this, owing to superficial irregularities but any uncertainty from this source would produce a smaller and opposite effect from that produced by the assumption previously made that the small quartz particles employed in the adsorption measurements were perfect spheres. The volume of the solution in the flask was taken as 2.8 liters on the average.

The number of equivalents of potassium chloride adsorbed by the surface of the cell from one liter of a 0.001 N KCl solution will therefore be $1030 \times 8.8 \times 10^{-12}/2.8 = 3.1 \times 10^{-10}$ equivalents and the adsorption correction in per cent. will amount to

$$P_A = \frac{3.1 \times 10^{-8}}{0.001} = 3.1 \times 10^{-6} \tag{53}$$

at this concentration. At lower concentrations the actual amount of potassium chloride adsorbed will be less than that adsorbed from a 0.001 N solution so that we may write in general

$$P_A < \frac{3.1 \times 10^{-8}}{C}. \tag{54}$$

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For the lowest concentration measured in this investigation the above relation gives

$$P_A < \frac{3.1 \times 10^{-8}}{2 \times 10^{-5}} < 0.015\%. \qquad (55)$$

We may therefore conclude that the adsorption correction for quartz will be negligible for all the solutions employed in this investigation.

5. Discussion of the Results.

(*a*) **The Experimental Error.**—The accuracy to be expected in the equivalent conductance Λ_C may be estimated from a consideration of the errors in the elementary terms entering into the calculation of this quantity. Resolved into its fundamental terms the expression for Λ_c is as follows:

$$\Lambda_c = \frac{74560\ k_c}{D} \frac{\left(1 - \frac{R_{Sl}}{R_W} W_{Sl}\right)}{W_S \cdot R_{Sl}} \qquad (56)$$

where D is the density of the solution, W_S is the weight of the salt in grams, W_{Sl} is the weight of the solution in kilograms, R_{Sl} is the resistance of the solution in the cell and R_W is the resistance of the water in the cell, k_c being the cell constant. Now in comparison with the errors in the quantity W_S, the weight of the salt, the errors in all of the other quantities involved are practically negligible. With the balance employed in this investigation, errors in the weight of the salt crystals added to the cell

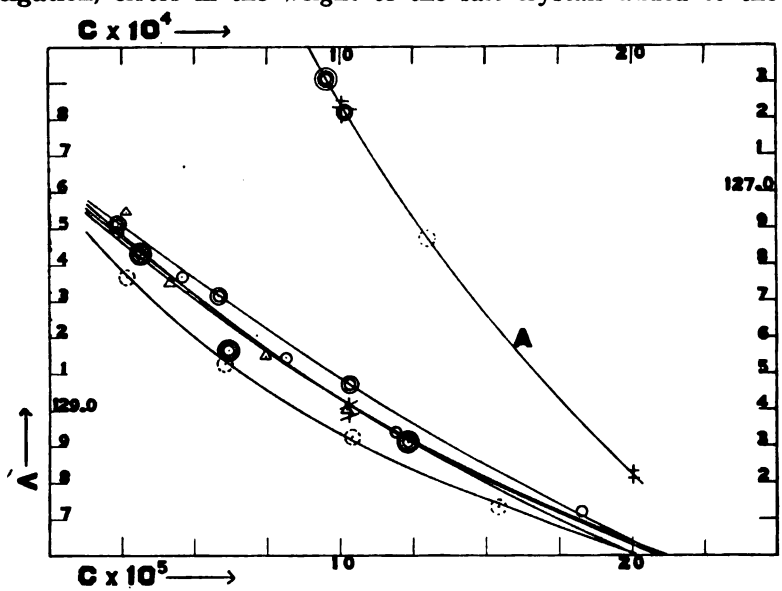

Fig. 10.—For Curve A, the scale of abscissas is indicated at the top of the diagram and the scale of ordinates at the right of the diagram. The small crosses indicate positions of points found by Kohlrausch and Maltby.

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might have amounted to as much as 0.05% at the highest dilutions measured and errors in the measured values of Λ_c as large as 0.05% are therefore to be expected.

(*b*) **Consistency of the Data.**—The data obtained in the five series of experiments are displayed graphically in Fig. 10, values of Λ_c being expressed as ordinates and values of the concentration as abscissas, the scale of abscissas for Curve A being indicated at the top and the scale of ordinates at the right of the diagram. The points for the five different series of experiments are indicated by certain symbols which will be used to distinguish the different series in all of the diagrams employed in the rest of this paper.

Owing to slight changes in the cell constant between two successive series, on account of the washing, handling, etc., of the electrodes, the points obtained in the different series do not lie upon any one smooth curve. Each series was therefore treated separately and a "best" smooth curve was drawn independently through its own points, giving the five curves shown in the figure. Of the five series shown that of March 6th seemed to be inconsistent with the other four and for this reason it will be disregarded in the discussion which follows, and the theoretical considerations will be based upon the values of Λ_c found in the other four series. In Table V are

TABLE V.

Equivalent Conductances at Round Concentrations as Obtained from the Smooth Curve of Each Series of Experiments.

Date.	Concentration × 10^4.			
	0.2.	0.5.	0.75.	1.0.
Jan. 24	129.515	129.320	129.170	129.030
Feb. 2	129.510	129.317	129.150	129.015
Feb. 10	129.537	129.360	129.220	129.080
Feb. 24	129.500	129.324	129.165	129.020
Mar. 6	129.427	129.190	129.04	128.93
Average[1]	129.515	129.324	129.176	129.036

shown the values of Λ_c for *round concentrations* as read off from the smooth curve for each of the individual series of experiments, together with the averages calculated from the first four series, the values for the fifth series being excluded as explained above.[2]

In Fig. 11 the observed valves for the first four series are shown, together with the locus of what seemed to be the "best smooth curve" which could be drawn through all of the points. A different and in general a

[1] March 6th data not included in average.

[2] The inclusion of the values for the series of March 6th would not change the calculated averages by more than 0.02% in any case.

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preferable method of locating such a "best curve" was devised later and is discussed below.

(*c*) **Calculationof Λ_0 and of K_0.**—In order to determine the values of these important constants the method devised by Washburn and described in the preceding paper was employed. In this method values of K_E, the Mass-Action expression, were plotted against corresponding values of C, each series of measurements being treated independently. The advantage of treating each series independently instead of employing average values lies in the fact that while the conductivity values them-

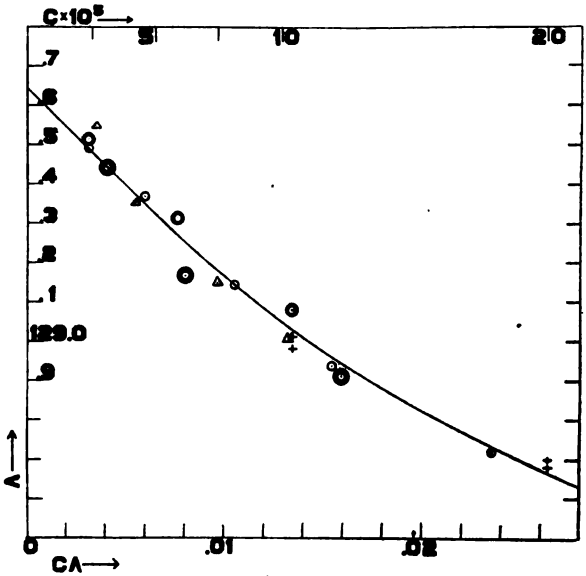

Fig. 11.

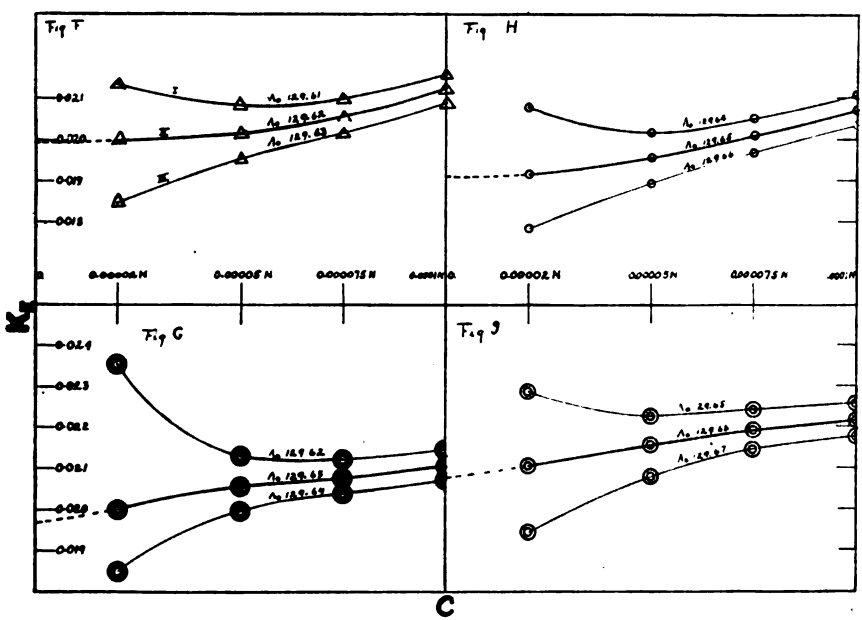

Fig. 12.—The determination of Λ_0 and K_0 values for the individual series of experiments.

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selves for the different series may differ slightly, owing to changes in the cell constant, such changes in the cell constant would be without influence upon the values of K_E since the value of the cell constant cancels out of the Mass-Action expression. Values of the Mass-Action expression K_E were computed for each of the first four runs, for the four concentrations shown in Table V, the Λ_c values being taken from that table. Fig. 12 shows the results of this procedure.

From an examination of this figure it is evident that each series of measurements independently fixes a K_o value and a Λ_o value, with a precision of at least 5 per cent. in the case of the former and of at least 0.01 per cent. in the case of the latter. In Table VI are summarized these values of Λ_o and K_o, together with the mean values, the average deviation from this mean and the final values adopted. For comparison, the set of Λ_o values obtained by Bates' method of extrapolation (see the preceding paper, p. 130) when applied to the same data is also included in this table.[1]

TABLE VI.

Summary of Λ_o and K_o Values from the Four Series of Measurements.

Date of series.	Λ_o.	*d*.	K_o.	*d*.	Λ_o. Bates' method.
Jan: 24	129.650	0.012	0.0192	0.0011	129.650
Feb. 2	129.620	0.018	0.0199	0.0004	129.615
Feb. 10	129.655	0.017	0.0212	0.0009	129.646
Feb. 24	129.627	0.011	0.0210	0.0007	129.614
Mean	129.638	0.015	0.0203	0.0008	129.631
Best value	**129.64**	**±0.02**	**0.020**	**±0.001**	

(*d*) **Conductance Values at Round Concentrations.**—A set of Λ_c values at round concentrations was obtained by interpolation from a large scale, $C\Lambda_c$-Λ_c, curve, the lower part of which is reproduced in Fig. 11. The values thus obtained are recorded in the author's thesis but will not be given here; instead a table of conductance values computed from the corresponding K_E values at round concentrations will be given. The curve from which the K_E values were interpolated was obtained by plotting the K_E values for all the measured points in the five series of experiments, and fitting a "best curve" to these points.[2] For the higher concentrations

[1] The rejected series (*i. e.*, that of March 6th) if treated in the same way gives for Λ_o the value 129.60 and for K_o the value 0.015. If these values were included in the general average, the averages for the five series would be, for Λ_o, 129.631 instead of 129.638 and for K_o 0.0192 instead of 0.0203.

[2] In computing the K_E values for the different series the Λ_o values employed in calculating the difference, $\Lambda_o - \Lambda$, were those corresponding to the data for the individual series in each instance rather than the finally adopted average of all the series. This method of calculation is necessary because the accuracy of K_E is determined entirely

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the K_E values were computed from the original data of Kohlrausch and Maltby.

The curve thus obtained is shown in Fig. 13. The heavy curve represents what is considered to be the locus of the "best smooth curve" through the points. The two boundary curves above and below this "best curve" represent the shift in the position of this curve which would be produced by a total error of 0.02% that is, by an error of 0.01% in the concentration

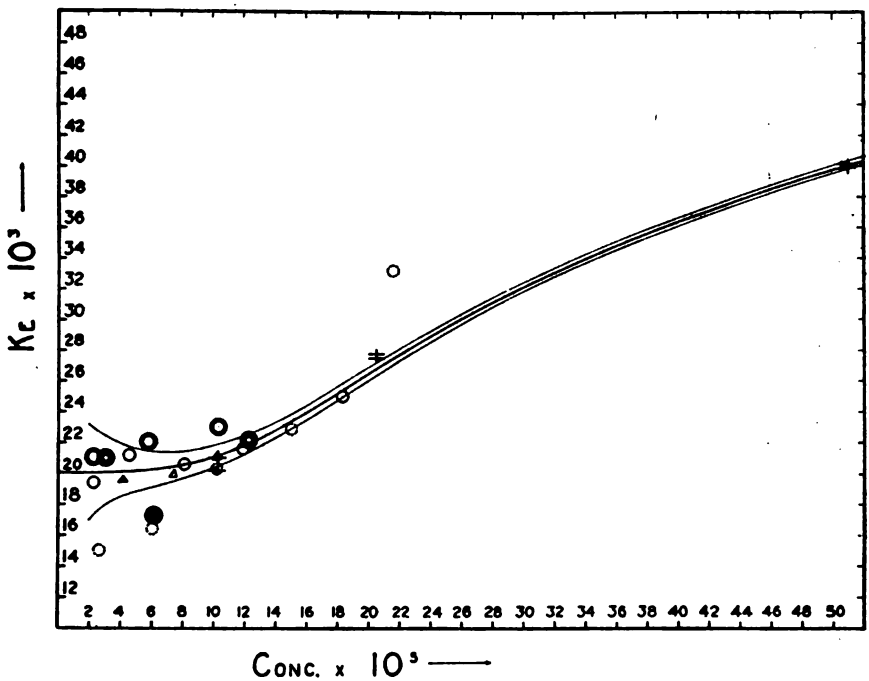

Fig. 13.—The variation of the mass-action expression K_E, with concentration, showing the locations of the observed values for each series of measurements. The crosses represent determinations by Kohlrausch and Maltby.

combined with an error of 0.005° in the temperature of the solution, for example. Since most of the observed points fall within the limits set by these two boundary curves it is evident that the agreement among them is even better than could reasonably have been expected considering all of the difficulties and chances of error involved in the work.

The interpolated K_E values for round concentrations together with the corresponding values of L, Λ_c, and α are given in Table VII. The values of Λ_c obtained in this way do not differ from those directly interpolated by the difference $\Lambda_0 - \Lambda$, and this difference must, therefore, be chosen for a given series of measurements so as to be consistent with that series, and to be independent of the cell constant.

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from the $C\Lambda$-Λ graph referred to above by more than 0.0046% on the average, the maximum difference being 0.015%. Differences of more than 0.01% occurred only four times. Interpolation from a K_E graph gives a rather more consistent set of data and is therefore to be preferred to any other graphical method of interpolating conductance data.

TABLE VII.

Conductance Data for Potassium Chloride Solutions at Round Concentrations. Temperature, 18.00°. Molecular Weight of Potassium Chloride, 74.560. "Cell Constant" Based upon the Value 0.01288 Reciprocal Ohms for the Specific Conductance at 25° of a Solution Composed of 7.43000 G. of Potassium Chloride in 1000 G. of Solution (Weights in Air).

I.	II.	III.	IV.	V.	VI.
Concentration (Millimol. per liter.) $C \times 10^3$.	True specific conductance $L \times 10^6$ (±0.02%).	Equivalent conductance Λ_c (±0.02%).	$\alpha = \frac{\Lambda_c}{\Lambda_0}$.	$1 - \alpha$.	$K_E = \frac{\alpha^2 C}{1 - \alpha}$.
0.00	0.0	129.64	1.0	0.0	0.020 ± 0.001
0.01	1.2957_3	129.57_3	0.9994_8	0.0005_{52}	0.0200_{00}
0.02	2.5902_2	129.51_1	0.9990_1	0.0009_{99}	0.0200_{02}
0.03	3.8833_8	129.44_6	0.9985_0	0.0015_{50}	0.0200_{03}
0.04	5.1753_6	129.38_4	0.9980_1	0.0019_{99}	0.0200_{06}
0.05	6.4660_0	129.32_0	0.9975_3	0.0024_{47}	0.0201_{4}
0.06	7.7554_9	129.25_8	0.9970_5	0.0029_{95}	0.0202_{2}
0.07	9.0437_9	129.19_7	0.9965_8	0.0034_{42}	0.0202_{5}
0.08	10.3309	129.13_8	0.9961_3	0.0038_{87}	0.0205_{0}
0.09	11.6172	129.08_1	0.9956_8	0.0043_{32}	0.0207_{0}
0.10	12.9029	129.02_9	0.9952_9	0.0047_{1}	0.0210_{2}
0.20	25.7356	128.67_6	0.9925_6	0.0074_{4}	0.0265_{0}
0.30	38.5353	128.45_1	0.9908_3	0.0091_{7}	0.0321_{0}
0.40	51.2976	128.24_4	0.9892_3	0.0107_{7}	0.0363_{3}
0.50	64.0240	128.04_8	0.9877_2	0.0122_{8}	0.0397_{2}
0.60	76.7214	127.86_9	0.9863_4	0.0136_{6}	0.0427_{8}
0.70	89.3970	127.71_0	0.9851_1	0.0148_{9}	0.0456_{3}
0.80	102.04_1	127.55_1	0.9838_9	0.0161_{1}	0.0480_{6}
0.90	114.66_0	127.40_0	0.9827_2	0.0172_{7}	0.0503_{4}
1.00	127.25_8	127.25_8	0.9816_3	0.0183_{7}	0.0524_{4}

(*e*) **Potassium Chloride and the Law of Mass Action.**—According to Fig. 13 potassium chloride obeys the law of the Mass Action within the experimental error up to a concentration of about 0.00007 N, in fact the value of K_E increases only about 5 per cent. between 0 and 0.0001 N. This contrasts strongly with the rapid increase of K_E at higher concentrations as illustrated by the data in Table VIII and the curves in Fig. 14. Thus for the first time, direct evidence has been obtained indicating that the ionization of a strong electrolyte in dilute solution takes places in accordance with the requirements of the law of Mass Action and that,

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TABLE VIII.

Illustrating the Rate of Increase of the Equilibrium Expression $K_E = \alpha^2 C/(1-\alpha)$ for a Tenfold Increase in Concentration, over Different Concentration Intervals.

C_1.	C_2.	K_{E_1}/K_{E_2}.
1.0	0.1	4.05
0.1	0.01	3.34
0.01	0.001	2.68
0.001	0.0001	2.49
0.0001	0.00001	1.05

except in degree, there is no difference between the behavior of strong electrolytes and weak electrolytes in this respect. Once having shown that the Mass-Action law is obeyed by strong electrolytes below a given concentration and once having obtained the value of K_e it is obvious that the conductance of such electrolytes in the concentration range below the limiting value in question can be accurately and certainly computed.

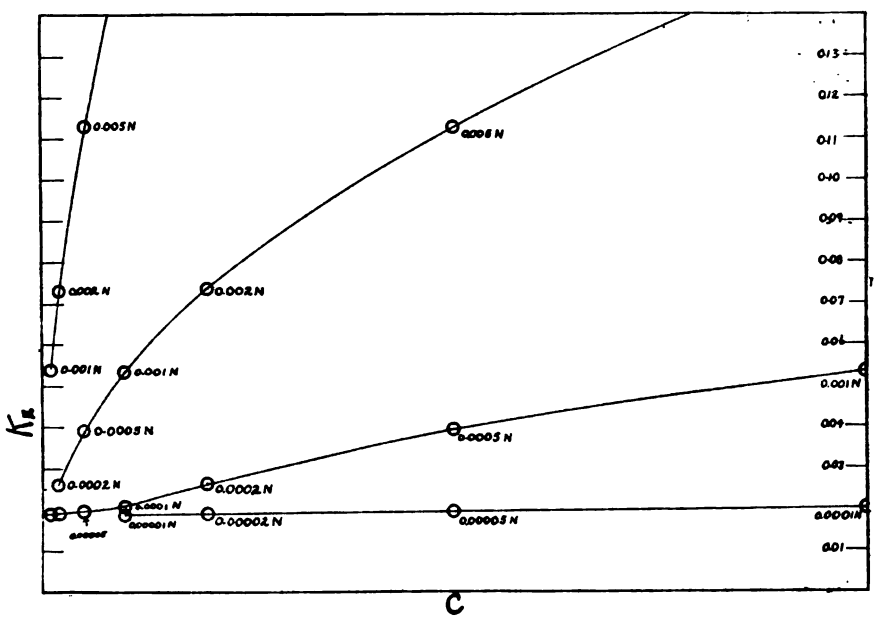

Fig. 14.—Illustrating the behavior of potassium chloride with respect to the mass-action law over different concentration ranges.

(*f*) **The Interpolation Equations of Kraus and of Bates.**—Kraus and Bray[1] found that the conductance for KCl between 0.001 N and 3 N could be satisfactorily represented by an equation which may be written in the form

[1] Kraus and Bray, THIS JOURNAL, 35, 1315 (1915).

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$$\log (K_E - K_o) = \log k + h \log (C\Lambda_c/\Lambda_o) \qquad (57)$$

where

$$K_E = \frac{\alpha^2 C}{1 - \alpha} = \frac{\Lambda_c^2 C}{\Lambda_o(\Lambda_o - \Lambda_c)} \qquad (58)$$

and K_o, k, h, and Λ_o represent the four parameters to be evaluated from the data.

Similarly, Bates[1] discovered that the same data between the concentrations 0.0001 N and 1 N could be very exactly represented by an equation which may be written in the form

$$\log (\log K_E/K_o) = \log k + h \log (C\Lambda_c/\Lambda_o) \qquad (59)$$

where K_o, k, and h, are the three parameters to be evaluated from the data, the value of Λ_o not being determined with reference to this equation but by an entirely different method.

It will be noted that in the form in which they are written above, both of these equations are linear functions and each should therefore give a straight line graph over the range in which it holds. It is interesting to compare these equations in this way with the results obtained in the present investigation which extend to lower concentrations than have ever been attained before. This comparison is made in Fig. 15. Values of log αC

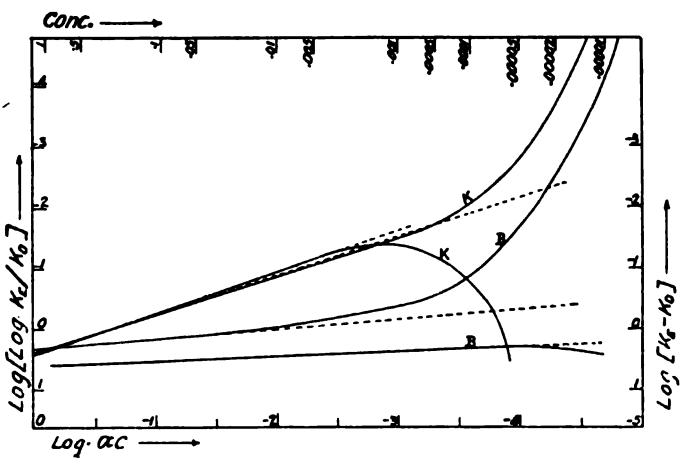

Fig. 15.—Illustrating the applicability of the interpolation equations of Kraus and of Bates, respectively, to the data for potassium chloride.

($= C\Lambda_c/\Lambda_o$ where Λ_c has been corrected for viscosity) are plotted as abscissae. The ordinates for the Kraus equation are shown on the right of the diagram and those for the Bates equation on the left. For convenience a scale of concentration is shown at the top of the diagram. The

[1] Washburn, "Principles of Physical Chemistry," 1915, p. 215, McGraw-Hill Book Co., New York.

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straight lines, which are shown dotted in the figure, mark the course which would be followed by the graph if the function were capable of expressing the data. These straight lines have in each instance been located with reference to the data for the higher concentrations.

The lower curve marked K is the curve of the Kraus equation using for Λ_0 and K_0 the values given by Kraus and Bray. It evidently begins to deviate from a straight line at about 0.005 N. If the "true values" of Λ_0 and K_0, as shown in Table VII, be employed in the Kraus equation, the lower curve marked K is obtained.

In the case of the Bates equation the lower curve marked B represents the graph of the equation using for Λ_0 and K_0 the values employed by Bates, and the upper curve marked B represents the graph of the same equation using for Λ_0 and K_0 the "true values" as given in Table VII. With the values employed by Bates, his equation is seen to hold down to about 0.00004 N but it fails below that concentration. With the "true values" of these quantities the equation begins to fail at about 0.03 N.

Fig. 15 demonstrates clearly that neither of these functions is capable of expressing the data in the lowest portions of the concentration range. Owing to its form the Bates equation is very sensitive to changes in the value of the K_0 parameter and similarly the Kraus equation is sensitive to changes in the constant Λ_0.

No attempt has been made to fit a single function to the whole K_g curve nor is there any necessity of deriving such a function since the Mass-Action law fits the lower part of the curve accurately and the remainder of the curve up to 1 N can be accurately expressed by Bates' interpolation equation, using the parameters employed by him.

6. Summary.

I. Conductivity water with a specific conductance of (0.053–0.070) $\times 10^{-6}$ reciprocal ohms at 18° has been prepared in large quantities by a single distillation of ordinary conductivity water from a quartz still into a quartz cell. This distillation was carried out in air free from carbon dioxide and ammonia.

II. A quartz cell of about three liters' capacity, provided with electrodes in the form of two co-axial platinum cylinders and so constructed that nothing but quartz or platinum comes into contact with the water, has been designed and constructed for measuring the conductivity of the water and of salt solutions prepared in it.

III. Potassium chloride solutions ranging in concentration from 0.00002 N to 0.001 N have been prepared in this conductivity water out of contact with the atmosphere by the successive introduction into the cell of small crystals of salt weighing about 0.005 g. The electrical conductivities of these solutions have been measured and their equivalent conductances calculated.

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IV. In order to ascertain the magnitude of the concentration change due to the adsorption of the salt on the walls of the cell, the specific adsorption of potassium chloride was determined by the use of a large quantity of quartz fragments. This was accomplished by observing the conductivity of 0.001 N to 0.0005 N solutions of potassium chloride in a special quartz cell before and after the addition of a definite quantity of well cleaned quartz fragments. Knowing the magnitude of the surface of the fragments and the surface of the cell, the maximum concentration change resulting from adsorption has been calculated and found to be negligible.

V. The values of Λ_c at round concentrations have been tabulated over the concentration range 0.00001 N to 0.001 N Table VII. The value of Λ_0 was found to be 129.64×0.02 as an average of four determinations.

VI. The Mass-Action "constant" K_E has been found to approach a constant value as the solution becomes sufficiently dilute. The limiting value at zero concentration was found to be 0.020×0.001. The relative increase of K_E for a tenfold increase in concentration over different regions of the concentration range is shown graphically in Fig. 14.

VII. The empirical equations of Bates and of Kraus, employed to express the relation between equivalent conductance and concentration, have been tested between the concentrations zero and 0.005 N and have been found not to be capable of expressing the conductivity data throughout this range.

The author wishes to express his thanks and gratitude to Professor E. W. Washburn under whose direction this investigation has been carried out. At all times his visits to the laboratory have been a source of help and inspiration.

Thanks are also due him together with his associates J. E. Bell, C. J. Baker and Karr Parker who contributed materially in solving the preliminary difficulties of this problem, without which it could not have been carried to a successful conclusion.

URBANA, ILL.

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF ILLINOIS. PUBLICATION NO. 32.]

THE EQUIVALENT CONDUCTANCE OF ELECTROLYTES IN DILUTE AQUEOUS SOLUTION.

IV. TWO LAWS GOVERNING THE IONIZATION EQUILIBRIUM OF STRONG ELECTROLYTES IN DILUTE SOLUTIONS AND A NEW RULE, BY MEANS OF WHICH THE EQUIVALENT CONDUCTANCE AT INFINITE DILUTION CAN BE DETERMINED FROM A SINGLE CONDUCTANCE MEASUREMENT.

BY EDWARD W. WASHBURN.

Received September 25, 1917.

CONTENTS.—1. Statement of the Two Laws. 2. The First Law. 3. The Second Law. 4. A General Rule for Determining Λ_0 Values from a Single Conductance

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Measurement. 5. Strong Acids and Bases and Salts of Weak Acids and Bases. 6. Ion Conductances.

1. Statement of the Two Laws.—With the aid of the conductance data for potassium chloride presented in the preceding paper, together with a study of the most accurate of the conductance data for other salts, obtained by Kohlrausch and his associates, it becomes possible to establish two general laws with reference to the behavior of strong electrolytes in dilute solutions. These laws may be stated as follows:

1. In sufficiently dilute solution (*i. e.*, for most practical purposes below $C = 0.0001\ N$, the increase of K_E between 0 and $0.0001\ N$ being only 1.05 fold) all uni-univalent salts of strong acids and bases obey the Mass-Action law and all of them have the same ionization constant.

2. In sufficiently dilute solution the values of the Mass-Action expression (and hence also the degrees of ionization) for all such salts are identical, the identity in the case of any two salts persisting up to higher concentrations the more nearly the salts under comparison resemble each other, and in any case persisting, within the experimental error of the data now available, up to $C = 0.0002\ N$ for all salts which have been carefully measured below this concentration. In the case of two salts such as potassium chloride and bromide for example, which resemble each other very closely, this identity persists up as high as $0.005\ N$.

2. The First Law.—Direct and unequivocal evidence that strong electrolytes obey the law of Mass Action in aqueous solutions in portions of the concentration range open to direct measurement is given for the first time by the data presented in the preceding paper.[1] It has been held by several observers that strong electrolytes would obey the Mass-Action law in sufficiently dilute solutions, in fact this statement has been explicitly made by Kraus and Bray, by Arrhenius, by Drucker, Tarle and Gomez and by Muller and Romann, although it seems to the writer that in none of these instances was the evidence employed by the investigators of a very decisive character.

The author's reasons for regarding as indecisive the evidence offered

[1] The theoretical basis of the Mass-Action law for a sufficiently dilute solution being almost purely thermodynamic in character, there would seem to be no necessity for additional evidence as to its validity for *all* classes of electrolytes at extreme dilutions. Such a view seems to the writer entirely sound and the value of the long desired "direct demonstration" furnished by the present investigation is not so much its conclusive evidence regarding the fact as it is its value as a discovery of the actual concentration range over which the law holds true within comparatively small known limits. As far as direct evidence of the fact that there was nothing in the behavior of strong electrolytes which would justify the view held by Kohlrausch and others to the effect that these substances would *not* obey the Mass-Action law even at high dilutions is concerned, it seems to the writer that this evidence is very clearly furnished by such figures as the first four ratios in the last column of Table VIII of the preceding paper.

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by Kraus and Bray, insofar as it concerned aqueous solutions, have already been given in the second paper of this series. While indecisive and quantitatively quite erroneous in the case of aqueous solutions, the evidence presented by Kraus and Bray as to the behavior of electrolytes in other solvents than water, nevertheless pointed strongly to the conclusion that the behavior of salts in aqueous solution would be found to differ only in degree and not in kind from the behavior of such electrolytes in solvents of lower dielectric constant.

In the paper[1] already referred to, Arrhenius reached the conclusion that uni-univalent salts obey the Mass-Action law up to about 0.0002 N and that they all have the same ionization constant, basing his conclusion upon some measurements of Kohlrausch and Maltby with very dilute solutions of sodium chloride and nitrate. After applying a metathesis correction to these data he found that the values so corrected obeyed the law of Mass Action. It seems to the writer, however, that his conclusion is quite unjustified by the evidence which he presents, for the following reasons: First, The metathesis corrections which he applied were incorrect both in magnitude *and in sign* is explained in the second paper of this series. Second, The metathesis corrections at these high dilutions are very much smaller than the accidental experimental errors of the data themselves and consequently could not be significant in any case. Third, The Λ_0 value employed by Arrhenius was incorrect as was also, consequently, the K_E values computed from it.[2]

Wegscheider's attempt[3] to show that salts obeyed the Mass-Action law up to about 0.03 N involved the use of an erroneous infinity value and the rejection of certain conductance values which are now known to be correct. Morever, salts actually do not obey the law over the concentration interval given by Wegscheider but only over an interval entirely outside of that covered by any data accessible to him. Substantially the same statement may be made concerning the reasoning of Drucker, Tarle and Gomez[4] and of Muller and Romann.

3. **The Second Law.**—The second law is an extension of the first one in that it postulates for different electrolytes the identity of the values of K_E (and hence also of α) even above the concentration range within which the Mass-Action law is obeyed. In other words, according to this law, those influences, which in case of strong electrolytes cause them to depart from the Mass-Action law at the higher concentrations, begin to be prac-

[1] *Loc. cit.*, pp. 11, 12.

[2] On the basis of the second and third reasons just stated, Kendall (*Loc. cit.*) also points out that the evidence which Arrhenius presents cannot be considered as supporting his conclusion.

[3] *Z. physik. Chem.*, 69, 624 (1909).

[4] Drucker, Tarle and Gomez, *Z. Elektrochem.*, 19, 11 (1913); Muller and Romann, *Compt. rend.*, 157, 400 (1913).

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tically identical in their effects in the case of the different electrolytes before they disappear entirely.[1] This fact has considerable practical importance in that it enables us to derive a very convenient rule by means of which it is possible to calculate correct Λ_0 values from a conductance measurement at one concentration. The evidence upon which the two laws formulated above is based is obtained by deriving the rule in question and testing it in the case of all salts for which data are available.

4. A General Rule for Determining Λ_0 Values from a Single Conductance Measurement.—The second law stated above is expressed mathematically by the equation

$$\frac{\Lambda_c^2 C}{\Lambda_0(\Lambda_0 - \Lambda_c)} = K_E \tag{60}$$

where the value of K_E is independent of the nature of the salt and can therefore be read off from the curve in Fig. 13, or taken from Table VII of the preceding paper (or preferably from a similar curve or table for a salt resembling as closely as possible the one under examination). Solving this expression we find

$$\Lambda_0 = \Lambda_c(1 + \Lambda_c C/\Lambda_0 K_E) \tag{61}$$

or with sufficient accuracy

$$\Lambda_0 = \Lambda_c(1 + C/K_E), \tag{62}$$

an expression by means of which the value of Λ_0 for any salt can be computed from a single value of Λ_c for that salt. Or since $1 + C/K_E = \alpha$ and equality of K_E values also implies equality of α values, the above equation may also be written

$$\Lambda_0 = \Lambda_c/\alpha \tag{63}$$

where α is independent of the nature of the salt.

It is evident that this method of calculating Λ_0 gives a result which possess exactly the same percentage accuracy as that possessed by the Λ_c value employed.

A convenient value of C to employ generally for this purpose is $C = 0.0001\ N$ and for this concentration and 18° the above expressions become

$$\Lambda_0 = 1.00475\ \Lambda_{0.0001} \tag{64}$$

or stated in words: *The Λ_0 value for every uni-univalent salt of a strong acid and base at 18° is 0.475% greater than its equivalent conductance at 0.0001 N.*

In order to demonstrate the validity of the assumption that in sufficiently dilute solutions all uni-univalent salts have identical values for their equilibrium expressions, it is only necessary to show for a sufficient number of

[1] Cf. Noyes and Falk, *Loc. cit.*, pp. 475 and 476, where the approximate (*i. e.*, to about 0.5%) identity of the α values for uni-univalent salts is pointed out. The identity of the K_E values postulated above, however, involves a *very much* closer identity of α values than that comtemplated in the statement of Noyes and Falk.

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TABLE IX.

Illustrating the calculation of Λ_o values for typical uni-univalent salts by means of the general relation $\Lambda_o = \Lambda_c(1 + C/K_E)$ and demonstrating the identity of the K_E values of all such salts up to $C = 0.0001\ N$. (Measurements by Kohlrausch and Maltby, corrected (+0.02%) for metathesis but not for atomic weights.)

$C \times 10^4$. Equivalents per liter.	NaCl.		KNO_3.		LiCl.		$LiNO_3$.	
	Λ_c.	Λ_o.	Λ_c.	Λ_o.	Λ_c.	Λ_o.	Λ_c.	Λ_o.
	108.20	108.72	125.48	126.09	98.17	98.63	94.48	94.92
1.037	108.11	108.63	125.54	126.15	98.11	98.57	94.44	94.88
	108.04	108.57						
$K_E = 0.0212$	Mean,	108.64 ± 0.05	Mean,	126.12 ± 0.03	Mean,	98.60 ± 0.01	Mean,	94.90 ± 0.02
	107.83	108.65	125.16	126.11	97.85	98.58	94.16	94.90
2.053	107.82	108.64	125.22	126.17	97.86	98.59	94.14	94.88
	107.82	108.64						
$K_E = 0.0268$	Mean,	108.64 ± 0.01	Mean,	126.14 ± 0.03	Mean,	98.59 ± 0.01	Mean,	94.89 ± 0.01
0.5212 $K_E = 0.02017$	108.41	108.69						

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salts that the Λ_0 values calculated from Equation 62 or 63 are independent of the concentration employed, for at least two concentrations sufficiently removed from each other. In order to make this test of the law the conductance data of Kohlrausch and Maltby for four salts at the two lowest concentrations measured were employed to calculate Λ_0 values, with the results shown in Table IX. These results show that within the experimental error the rule gives for these salts the same Λ_0 value for the two concentrations 0.0001 N and 0.0002 N respectively, and in one instance where such measurements were available also for the concentration 0.00005 N. In this table the *individual conductance values* for the different concentrations have been employed instead of the rounded values obtained from a smooth curve, in order to show the degree of concordance of the measurements among themselves, and consequently the degree of concordance which might be expected for the Λ_0 values.

Using interpolated values at round concentrations and 1911 atomic weights as given by Noyes and Falk, a similar table has also been prepared

TABLE X.

Illustrating the calculation of Λ_0 values for typical uni-univalent salts by means of the relation, $\Lambda_0 = c(\Lambda_1 + (C/K_E))$. The data employed are taken from the tables compiled by Noyes and Falk (THIS JOURNAL, 34, 461 (1912)). A metathesis correction[1] of +0.02% has been applied for concentrations 0.0001 and 0.0002 and one of +0.01% for concentrations 0.0005 and 0.001 N. The values of Λ_c given below have also been corrected for viscosity where this correction is appreciable. The values in parenthesis in the first column have been selected as the "best" Λ_0 values. Salts in which either the acid or base is "weak" are excluded because the Λ_c values recorded in the literature are incorrect.

Salt.	$C \times 10^4$.	Λ_c.	$\Lambda_0 - \Lambda_c$.	Λ_0.	Salt.	$C \times 10^4$.	Λ_c.	$\Lambda_0 - \Lambda_c$.	Λ_0.
NaCl	1	108.05	0.513	108.56	$NaNO_3$	1	104.47	0.50	104.97
(108.57)	2	107.77	0.806	108.576	(104.95)	2	104.11	0.78	104.89
	5	107.12	1.33	108.45		5	103.54	1.29	104.83
	10	106.44	1.99	108.43		10	102.76	1.92	104.68
	20	105.50	2.83	108.33		20	101.81	2.72	104.53
	50	103.76	4.39	108.15		50	99.99	4.24	104.25
LiCl	1	97.98	0.464	98.44	KNO_3	1	125.42	0.59	126.01
(98.42)	2	97.69	0.734	98.42	(126.02)	2	125.10	0.94	126.04
	5	97.02	1.206	98.23		5	124.35	1.55	125.90
	10	96.36	1.80	98.16		10	123.56	2.31	125.87
	20	95.47	2.55	98.02		20	122.50	3.29	125.78
	50	93.82	3.96	97.78		50	120.38	5.12	125.48
RbCl	1	132.3	0.63	132.9	$LiNO_3$	1	94.32	0.44	94.76
(132.9)	2	(131.9)	0.99	132.9	(94.78)	2	94.01	0.71	94.72
	5	(131.2)	1.63	132.8		5	93.38	1.17	94.55
	10	130.3	2.44	132.7		10	92.74	1.73	94.47
						20	91.84	2.46	94.30
						50	90.26	3.82	94.08

[1] Cf. the first paper of this series, Sec. 8, p. 119.

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TABLE X (*continued*).

Salt.	$C \times 10^4$.	Λ_c.	$\Lambda_o - \Lambda_c$.	Λ_o.	Salt.	$C \times 10^4$.	Λ_c.	$\Lambda_o - \Lambda_c$.	Λ_o.
CsCl	1	132.2	0.63	132.8	$AgNO_3$	1	115.03	0.54	115.57
(132.90)	2	131.9	0.99	132.9	(115.6)	2	114.58	0.86	115.44
	5	131.25	1.63	132.88		5	113.89	1.41	115.30
	10	130.55	2.45	132.90		10	113.15	2.12	115.27
	20	129.38	3.49	132.87		20	112.07	3.01	115.08
	50	127.33	5.43	132.76		50	110.03	4.66	114.69
KBr	1	131.07	0.62	131.69	$KClO_3$	1	118.65	0.56	119.21
(131.71)	2	130.78	0.98	131.76	(119.25)	2	118.37	0.89	119.26
	5	130.06	1.62	131.68		5	117.69	1.46	119.15
	10	129.29	2.42	131.71		10	116.93	2.19	119.12
	20	128.22	3.46	131.68		20	115.84	3.10	118.94
	50	126.31	5.39	131.70		50	113.84	4.81	118.65
KI	1	129.78	0.62	130.40	$KBrO_3$	10	109.9	2.06	111.96
(130.65)	2	129.52	0.97	130.49	(112.0	20	108.7	2.92	111.62
	5	128.98	1.61	130.59	±0.1)	50	106.9	4.54	111.4
	10	128.24	2.41	130.65					
	20	127.19	3.43	130.62					
	50	125.28	5.35	130.63					
KSCN	1	120.15	0.57	120.72	$NaIO_3$	1	76.71	0.36	77.07
(120.8)	2	119.95	0.90	120.85	(77.05)	2	76.46	0.57	77.03
	5	119.30	1.48	120.78		5	75.84	0.94	76.78
	10	118.56	2.22	120.78		10	75.20	1.40	76.60
	20	117.57	3.16	120.73		20	74.33	1.98	76.31
	50	115.73	4.99	120.72		50	72.69	3.04	75.73
KIO_3	1	97.66	0.464	98.12	$LiIO_3$	1	66.68	0.31	66.99
(98.12)	2	97.36	0.73	98.09	(66.92)	2	66.45	0.50	66.95
	5	96.73	1.20	97.93		5	65.88	0.82	66.70
						10	65.29	1.21	66.51
						20	64.47	1.71	66.18
						50	62.99	2.67	65.66

for all uni-univalent salts of strong acids and bases for which reliable data are available, the calculations being carried up as high as $C = 0.005\ N$ in many cases. The results are shown in Table X. It will be seen that in every instance, with the possible exception[1] of silver nitrate there are at least two concentrations which give within the experimental error the same Λ_o values. The values of K_E upon which the table is based are those for potassium chloride and it will be noticed that in the case of potassium bromide, potassium chloride, rubidium chloride and potassium thiocyanate the identity of the K_E values persists up as high as 0.005 N in several cases.

[1] In view of the Bureau of Standards' investigation of the behavior of this salt and its solutions (Bur. Standards, *Scientific Paper* 285), I think the accuracy of the conductivity data for $AgNO_3$ may be fairly questioned.

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In the case of potassium iodide the table also indicates a strong probability that the conductance data given for this salt below 0.001 N are too low.

An example may also be given of the calculation of Λ_0 when the largest Λ_c available is that for $C = 0.001$ N. Suppose it is desired to calculate the Λ_0 value of lithium iodate from the conductance value, $\Lambda_{0.001} = 65.29$. The K_E value for potassium chloride cannot be employed here as the concentration is too high. Instead we will base the calculation upon the α value of sodium iodate at 0.001 N which we can calculate from the data in Table X and find to be 75.30/77.05. Whence from Equation 63 we find Λ_0 for lithium iodate to be 66.93 as against 66.92 given in Table X. Such a calculation as this is of course only trustworthy when the comparison salt resembles very closely the one whose Λ_0 value is being sought.

5. Strong Acids and Bases and Salts of Weak Acids and Bases.—The reason why strong acids and bases themselves as well as salts of weak acids and bases have not been included within the scope of the laws formulated above is not because there is any reason to suppose that these substances form exceptions to the laws, but merely because there exist no reliable data for testing the laws in any of these cases, nor can such data be secured except by employing ultra-pure conductivity water, as explained in Sec. 9 and 11 of the first paper of this series. In view of the great importance of securing reliable Λ_0 values for acids and bases it is highly desirable that the work begun with potassium chloride should be extended to these substances as well as to salts of weak acids and bases and to salts of higher valence types. The availability of ultra-pure conductivity water opens an entirely new field to accurate investigation and it is practically certain that the extension of the work would yield for the above classes of substances results and laws fully as important and interesting as those obtained by the study of potassium chloride. The special Conductivity Laboratory in the new chemistry building at the University of Illinois was designed and equipped especially for this work and its equipment is probably not equaled anywhere else at the present time. Unfortunately, however, there seems to be no present prospect that the work will be continued.

TABLE XI.

Illustrating Kohlrausch's law of the independent migration of ions. Differences in ion conductances for four pairs of ions, as calculated from the "best" Λ_0 values shown in Table X.

Salts.	$\Lambda_1-\Lambda_2$.	Salts.	$\Lambda_1-\Lambda_2$.	Salts.	$\Lambda_1-\Lambda_2$.	Salts.	$\Lambda_1-\Lambda_2$.
KCl-NaCl	21.07	NaCl-$NaNO_3$	3.62	KCl-LiCl	31.22	NaCl-$NaIO_3$	31.52
KNO_3-$NaNO_3$	21.07	KCl-KNO_3	3.62	KNO_3-$LiNO_3$	31.24	KCl-KIO_3	31.52
KIO_3-$NaIO_3$	21.07	LiCl-$LiNO_3$	3.64	KIO_3-$LiIO_3$	31.20	LiCl-$LiIO_3$	31.50
Mean,	21.07	Mean,	3.63	Mean,	31.23	Mean,	31.51

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6. Ion Conductances.—From the "best" values given in Table X the differences in ion conductances for the four pairs of ions shown in Table XI have been calculated. From the mean values of these differences, together with the other Λ_0 values given in Table X, the set of ion conductances shown in Table XII has been calculated. These values are based upon 0.4960 as the cation transference number for potassium chloride.

TABLE XII.

Ion Conductances at 18°.

Ion	K.	Na.	Li.	Rb.	Cs.	Ag.	Cl.	NO_3.
Λ	64.30	43.23	33.07	67.6	67.56	53.9	65.34	61.71
Ion	IO_3.	Br.	I.	SCN.	ClO_3.	BrO_3.		
Λ	33.83	67.41	66.35	56.5	54.95	47.7		

URBANA, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA.]

EQUILIBRIUM DATA ON THE POLYBROMIDES AND POLYIODIDES OF POTASSIUM.

BY G. A. LINHART.

Received November 12, 1917.

I. The Equilibrium between Bromine and Potassium Bromide Solutions at Different Temperatures.

In connection with an investigation dealing with the polyiodides of potassium, it was of interest to calculate for comparison the values for the equilibrium constants of the polybromides from Worley's data[1] at 26.5° and compare them with those obtained by Jones & Hartmann[2] at 0°. From these values at 0° and 26.5°, were then calculated equilibrium constants for 32.6° and compared with those calculated from Worley's data for 32.6°. In Table I are given Worley's data at 26.5° and the equilibrium constants calculated from them with the aid of the following relations:

$$\frac{(Br^-)}{\gamma} + \frac{(Br_3^-)}{\gamma} + \frac{(Br_5^-)}{\gamma} = \Sigma(KBr), \quad (1);$$

$$\frac{(Br_3^-)}{\gamma} + \frac{2(Br_5^-)}{\gamma} + (Br_2) = \Sigma(Br_2), \quad (2);$$

$$\frac{(Br_3^-)}{(Br^-)(Br_2)} = K', \quad (3); \qquad \frac{(Br_5^-)}{(Br_3^-)(Br_2)} = K'', \quad (4)$$

Combining (2) and (4) we have,

[1] *J. Chem. Soc.* (*London*), **87**, 1107 (1905).

[2] *Trans. Am. Electrochem. Soc.*, 30, 295 (1916).

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$$\frac{(Br_5^-)}{\gamma} = \frac{\Sigma(Br_2)-(Br_2)}{\left(\frac{I}{K''(Br_2)} + 2\right)} \quad (5).$$

It is here assumed that for moderate concentrations of KBr, KBr_3 and KBr_5, the thermodynamic degrees of dissociation, γ, of these substances are the same in the mixture, and also that the activity of the free bromine is proportional to its concentration. The validity of this latter assumption is substantiated by the vapor-pressure measurements of Br_2 aq. by Winkler.[1] It is to be noted that the constants so calculated are fairly concordant.

It was found by trial that if 1.2 is taken for the value of K'',[2] the following values were obtained for K':

TABLE I.

$K''=1.20$. Series A. ΣKBr = 0.5 gram-mol per liter.			$t=26.5°$ C. Series B. ΣKBr = 0.1 gram-mol per liter.		
$\Sigma(Br_2)$.	Free (Br_2).	K'.	$\Sigma(Br_2)$.	Free (Br_2).	K'.
0.51829	0.12507	15.8	0.23849	0.15455	14.4
0.48217	0.10583	17.5	0.21650	0.13515	15.9
0.46720	0.10431	16.8	0.18013	0.10647	16.3
0.45997	0.09712	17.7	0.17761	0.10532	15.7
0.42581	0.08508	17.6	0.16684	0.09644	16.3
0.42246	0.08714	16.5	0.14837	0.08516	14.6
0.37041	0.07352	15.2	0.13202	0.07215	15.9
0.32753	0.06008	15.6	0.08416	0.04173	15.6
0.29450	0.04999	16.2	0.06365	0.03027	15.2
0.28966	0.04818	14.9	0.04320	0.01938	15.3
0.21097	0.03249	15.5			
0.14892	0.02000	16.5			
0.11400	0.01515	15.6			
0.05700	0.00751	14.3			

The average of the 24 values for K' at 26.5° is 15.9 and the value for K' at 0° is 19.6,[3] whence ΔH, the heat of the reaction, $Br^- + Br_2(aq.) = Br_3^-$, equals —1290 cal., calculated by means of the equation

$$\ln K'_{T''}/K'_{T''} = \Delta H\,(T''-T')/RT''T', \quad (6)$$

Similarly, ΔH for the reaction $Br_3^- + Br_2(aq.) = Br_5^-$ equals —3390 cal., where K'' at 26.5° equals 1.20 and K'' at 0° equals 2.08.[4] By means of these values, the corresponding equilibrium constants were then calculated for 32.6°, giving for K' 15.2 and for K'' 1.06, on the assumption that ΔH remains constant for the given range of temperature.

[1] *Chem. Zeit.*, 23, 687 (1899).

[2] Since the equation for K'' contains the term (Br_2) to the second power it is found more advantageous to maintain K'' constant throughout the two series and calculate: first, the value for KBr_5 by means of Equation 5.

[3] Jones and Hartmann, already cited (page 326).

[4] *Ibid.*

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In Table III Col. 3 are given the values for K' at 32.6° calculated from Worley's data by means of Equations 5, 2, 1 and 3, keeping K'' constant at 1.06, which is the calculated value from equilibrium constants at 0° and 26.5° by means of Equation 6.

TABLE II.

$K'' = 1.06$. $t = 32.6°$ C.

$\Sigma KBr = 0.125$ gram-mol per liter.

$\Sigma(Br_2)$.	Free (Br_2).	K'.
0.22530	0.12800	15.7
0.21711	0.12094	16.5
0.18989	0.10202	15.7
0.13828	0.06838	14.7
0.11750	0.05446	15.9
0.07974	0.03423	15.3
0.04875	0.01974	14.6
0.01831	0.00698	14.0

The average value for K' at 32.6° (15.5) agrees fairly well with the value (15.2), calculated from K' at 0° and at 26.5°.

KBr Solutions Saturated with Respect to Bromine.—If we now apply the value 1.20 for the equilibrium constant K'' at 26.5° to Worley's data of KBr solutions saturated with bromine, the average value obtained for K' is found to be several per cent. too high. This may be due to the presence of another complex, KBr_7.[1] However, the oscillations of the ratios of the total combined bromine and total KBr to the extent of about 10% may account, in part, for this difference.

Summary.

(1) In Table III below are given values for the equilibrium constants K' and K'' calculated from experimental results at 0°, 26.5° and 32.6°, as well as calculated values for 25°.

TABLE III.

t°.	$\frac{(Br_7^-)}{(Br^-)(Br_2)}$.	$\frac{(Br_7^-)}{(Br_3^-)(Br_2)}$.
0.0	19.6	2.08
25.0	16.1	1.23
26.5	15.9	1.20
32.6	15.5	1.07

[1] Since, in saturated solution, with reference to bromine, the combined bromine is practically a linear function of the total KBr in the solution, concordant constants would be obtained for any number of complexes of the type $KBr.nBr_2$, which we may assume to exist together in the same solution, but the constants so obtained would not necessarily be of the same magnitude as those given in Table I. Worley also calls particular attention to the fact that the function is not quite linear from the experiments at 18.5°. This discrepancy is apparent only, for a 1% error in the solubility of bromine in water (which is quite within experimental error as contrasted with data of other investigators) would change the ratio when KBr = 0.01 from 1.86 to 2.30, while, when KBr = 0.9, the ratio would be changed only from 2.27 to 2.29.

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(2) The heat of the reaction $Br^- + Br_2(aq.) = Br_3^-$ equals —1290 cal., and of the reaction $Br_3^- + Br_2(aq.) = Br_5^-$ equals —3390 cal.

II. Distribution of Iodine between CCl_4 and H_2O, at 25°.

Experimental.—A concentrated solution of pure iodine in pure carbon tetrachloride was diluted with the desired amount of carbon tetrachloride and introduced into resistance bottles, of about 600 cc. capacity, provided with ground glass stoppers. The bottles were then filled to overflowing[1] with conductivity water. The stoppers were inserted and the bottles suspended up to the necks in a thermostat. After the bottles attained the temperature of the bath, 25°, the stoppers were tightened. The bottles were frequently shaken during the day and left in the thermostat overnight to reach equilibrium. On removing a bottle for analysis it was placed up to the neck in a vessel of water of the same temperature as that of the thermostat. A portion of the water phase was then siphoned into a weighed Erlenmeyer flask provided with a ground glass stopper. The siphons used for the CCl_4 phase were sealed at the bottom, terminating in a small, thin bulb, easily broken when in contact with the bottom of the bottle. The iodine was estimated in the usual way by means of sodium thiosulfate. The results are given in table below.

TABLE IV.—EXPERIMENTAL RESULTS AT 25°.

	Grams solution for analysis.		Gram iodine found in.		Mol iodine to 1000 g.		
	H_2O phase.	CCl_4 phase.	H_2O phase.	CCl_4 phase.	CCl_4 phase.	H_2O phase.	Ratio.
(a)	370.215	48.335	0.037760	0.280586	0.022988	0.000402	57.2
(b)		50.913		0.295012	0.022945		57.1
(a)	372.175	48.350	0.058916	0.429174	0.035260	0.000623	56.6
(b)		51.005		0.452255	0.035220		56.6
(a)	369.175	48.349	0.067887	0.496254	0.040828	0.000724	56.4
(b)		50.965		0.522943	0.040815		56.4
(a)	419.405	48.248	0.080340	0.522943	0.043020	0.000754	57.1
(b)		51.075		0.550811	0.042921		56.9
(a)	357.975	48.503	0.082416	0.623925	0.051304	0.000907	56.6
(b)		51.005		0.656383	0.051325		56.6

Discussion of the Results.

It is interesting to note that when the measurements of the distribution of iodine between carbon tetrachloride and water are performed with the necessary precautions, concordant ratios are obtained for the entire range of concentration, and that this value is equal to the one obtained from the solubility of iodine in carbon tetrachloride and water, respectively.

[1] This precaution was found necessary as the emulsion formed between the CCl_4 and the iodine, when the bottles were shaken, when there was an air space, led to erroneous results, because there was no equilibrium established even after the bottles had been left in the thermostat for several days, while, when there was no air space, the equilibrium was established very rapidly and the water phase became perfectly clear.

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Thus, according to Jakowkin [1] the solubility of iodine in carbon tetrachloride at 25° is 0.11941 mol per liter of solution, and the solubility of iodine in water is 0.00134 mol per liter of solution. Dividing the amount of iodine in the tetrachloride phase by the amount in the water phase we obtain a ratio of 89. Comparing this value with the one obtained from Expt. 4 in which the volumes of the CCl_4 phase used for analysis were 30.0 cc. and 31.7 cc., respectively, we obtain 90.7 and 90.4 or 90.6[2] while the ratios given by Jakowkin range from 89 at saturation to 85 at extreme dilution.

On account of the small solubility of iodine in water or in carbon tetrachloride it is immaterial in what units the concentrations are expressed, as the ratios remain reasonably constant, whether computed to mol fractions, mol per liter of solution, or mols per thousand grams of solvent.

Summary.

The results here presented show that the activity of iodine is proportional to its concentration in water and in carbon tetrachloride, from extreme dilution to saturation. It does not, of course, necessarily follow that because the distribution ratio of a substance between two immiscible solvents is constant, the activity and therefore the vapor pressure of the substance in each solvent is proportional to the mol fraction; *i. e.*, the vapor pressure of the substance need not obey either Raoult's law or Henry's law in the two solvents but may vary proportionately in the same direction and thus give a constant partition ratio.

III. The Equilibrium between Iodine and Potassium Iodide in Water Solution.

In Sec. I of this paper it is pointed out that the increase in the solubility of bromine in a water solution of KBr is proportional to the concentration of the KBr. This is not the case for the increase in the solubility of iodine in a water solution of KI. Thus, a liter of a 0.1 *M* KI solution dissolves about 0.05 *M* I_2, while a liter of a 1.0 *M* KI dissolves about 0.7 *M* I_2, the iodine separating out again on dilution with water. This may be explained by assuming that the higher complex compounds of KI and I_2 are chiefly of the type $2KI.nI_2$ instead of $KI.nI_2$ as in the case of the polybromides. In deciding on a value for n in the complex $2KI.nI_2$ it seemed most plausible as a first approximation to choose a value corresponding to the compound which has been investigated and identified by several investigators, *viz.*, 2KI, $6I_2$ or K_2I_{14}.[3] We then have,

$$\frac{(I^-)}{\gamma} + \frac{(I_3^-)}{\gamma} + \frac{2(I_{14}^{--})}{(\gamma)^2} = \Sigma KI, (1); \qquad \frac{(I_3^-)}{\gamma} + \frac{6(I_{14}^{--})}{(\gamma)^2} + I_2 = \Sigma I_2, (2);$$

[1] *Z. physik. Chem.*, 20, 19 (1896).

[2] This agrees with the value given by Bray and MacKay, THIS JOURNAL, 32, 1208 (1910).

[3] *Z. anorg. Chem.*, 50, 403 (1906); Foote and Chalker, *Am. Chem. J.*, 39, 561 (1908).

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$$\frac{I_3^-}{I^-} = (I_2)K', (3); \quad \frac{I_{14}^{--}}{(I_3^-)^2} = (I_2)^4K''.$$

Assuming that at 0.005 *M* KI the concentration of K_2I_{14} is zero, then $K'(I_2)K'$ equals 0.92. The values for K'' were then calculated, using the data given by Parsons and Whittemore for concentrated solutions. These are apparently the most reliable data on the solubility of iodine in concentrated water solution of KI with iodine as the solid phase. The data given by Abegg and Hamburger not only differ from those mentioned above, but are grossly inconsistent among themselves.

In the first column of Table V are given the concentrations of KI in mols per thousand grams of water; in the second column, the concentrations of the iodine also in mols per thousand grams of water; in the third column are given the equilibrium constants $(I_2)^4K''$.

TABLE V.

ΣKI.	ΣI_2.[1]	$(I_2)^4K''$. 25.°	
0.0050	0.00373	....	Bray & MacKay[2]
0.0500	0.02577	0.17	
0.1000	0.05135	0.18	
0.4136	0.2313	0.17	Linhart
0.5959	0.3538	0.18	
0.8065	0.5176	0.20	
1.0246	0.7079	0.21	
1.4747	1.1118	0.20	Parsons & Whittemore[3]
2.1952	1.9030	0.21	
3.3578	3.4595	0.23	
3.9349	4.4339	0.26	
6.9109	9.7669	0.29	
12.6880	20.9390	0.28	
17.2711	29.6126	0.24	

The concordance of the values in the last column is perhaps better than might be expected, when the mass law is applied to such concentrated solutions, and when it is assumed that the activity of the divalent salt K_2I_{14} is equal to the square of the activity of KI_3, which holds only approximately even for very dilute solutions.

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[1] 0.00132 mol, the solubility of iodine at 25° were subtracted from each value of column two. The corrected values were used in the calculation of the ratios given in column three.

[2] THIS JOURNAL, 32, 919 (1910).

[3] Parsons and Whittemore, *Ibid.*, 33, 1934 (1911).

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[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY.]

THE SOLUBILITY OF SODIUM SULFATE AS A MEANS OF DETERMINING TEMPERATURES.

BY THEODORE W. RICHARDS AND VICTOR YNGVE.

Received November 18, 1917.

The accurate fixing of temperatures is becoming more and more important in view of the increasing exactness of physico-chemical measurements. Among the definite points employed, those involving a single component, such as the melting point of ice and the boiling point of water under atmospheric pressure, are most common.[1] Quadruple points, or more strictly speaking, bicomponent transitions under definite pressure, such as the transition temperatures of hydrated salts, also serve excellently.[2] Other methods employing two components, such as the freezing points of dilute aqueous solutions,[3] or the floating equilibrium of a known float in a solution whose density is changed by adding an easily determined solute until an exact equilibrium is obtained at the temperature in question,[4] or a thermochemical method[5] may be used in emergencies.

Of course, any definite property of material possessing a large temperature coefficient could be used for this purpose. If the solubility of salts has not been used before (we can find no reference to its use), the reason has been, perhaps, a doubt concerning the certainty of obtaining exact saturation, and the lack of adequate data. Indeed, nearly, if not quite all, of the published results of this kind are not of the order of accuracy required.

In order that a salt may serve as a means of fixing temperatures with precision through the determination of its solubility at any point in question, it must possess a large temperature coefficient of solubility; its solutions must be easily saturated, but not easily supersaturated; it must be readily determinable quantitatively, and must not be difficult to obtain in a high degree of purity. Many substances possess three of these requirements. With regard to definiteness of saturation, we were guided by van't Hoff's experience that univalent metals are better than bivalent.[6]

[1] For a convenient list of recently found values of a number of such points, see Bureau of Standards, *Bull.* 35, Ed. 2 (1915).

[2] This method was first proposed in 1866, but the proposal was forgotten and buried. Apparently it was first applied practically in 1898. For references see Richards and Fiske, THIS JOURNAL, 36, 486 (1914); also p. 89 of this number.

[3] Richards and Jackson, *Proc. Am. Acad. Arts Sci.*, 41, 451 (1906).

[4] Richards and Shipley, THIS JOURNAL, 36, 1–10 (1914).

[5] Richards and Thorvaldson, THIS JOURNAL, 37, 81 (1915).

[6] One of the authors remembers having heard orally from van't Hoff that the latter came to this conclusion in the course of his work on the Stassfurt salts; a published reference to this conclusion has not yet been found.

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Sodium sulfate seemed to possess the necessary qualities in as happy conjunction as any, and it was accordingly chosen for detailed study.

Historical.

The solubility of sodium sulfate has been determined by many investigators. The determinations which are chosen as best by Landolt-Börnstein-Roth between the temperatures of 15° and 25° are those of Loewel[1] and the Earl of Berkeley.[2] Loewel's thermometer was not described in detail, but Lord Berkeley's had been standardized at Kew, and was doubtless better, although rendered somewhat doubtful by a slight uncertainty in the ice point. Neither of these series of measurements which are given below, is precise enough for the object in hand.

TABLE I.—EARLIER DATA CONCERNING THE SOLUBILITY OF $Na_2SO_4.10H_2O$ IN WATER.

	Na_2SO_4 in 100 g. H_2O.	
Temp.	Loewel.	Berkeley.
15.00	13.20	...
15.65	...	14.07
18.00	16.80	...
20.00	19.40	...
24.90	...	27.67
25.00	28.00	...

Purification of Materials.

In most of our determinations the purest water was used, prepared by redistilling ordinary distilled water, first from alkaline permanganate, and then from a trace of sulfuric acid with a block tin condenser. Ordinary laboratory steam-distilled water was used in a few trials, and gave exactly the same result for the solubility of sodium sulfate as did the purest water.

"Chemically pure" sodium sulfate was four times recrystallized in porcelain and drained in the centrifuge, a portion of the thrice recrystallized product being reserved for comparison. No difference could be found in the solubility of the two specimens; hence further crystallization was deemed unnecessary. Evidence of purity is also afforded by the fact that such material almost always gives a constant transition temperature, even after many further crystallizations.[3] Our experience thus shows that both water and sodium sulfate are easily obtained in a state pure enough for the purpose in hand.

The Experimental Procedure for Determining Solubility.

The method of procedure was chosen so that it might combine simplicity and ease of manipulation with the requisite degree of accuracy. Coarsely granular crystals, about 1 to 3 mm. in diameter, were placed

[1] Loewel, *Ann. chim. phys.*, [3] 49, 50 (1857).

[2] Berkeley, *Phil. Trans.*, (*A*) 203, 209 (1904).

[3] Richards and Wells, *Proc. Am. Acad. Arts Sci.*, 38, 435 (1902).

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in a wide test tube 3 cm. in diameter and 15 cm. long. Water was added to fill the tube to within 3 cm. from the top and a thoroughly cleaned rubber stopper was fitted to the opening. Thin wide rubber tubing was drawn over the rubber stopper and the lip of the test tube in order to keep the lip of the test tube dry. Finally the stopper was wired in place in order to prevent the possibility of its accidental dislodgement. The test tube was then secured by rubber bands to a strip of brass soldered at right angles to a revolving axle, and rotated in a thermostat which was maintained constant in temperature within 0.001°. This method attains saturation much more quickly than that which depends upon stirring the solution above resting crystals. The equilibrium is, of course, established only on the surface between the two phases, and the speed of its attainment is accelerated by promoting diffusion and convection immediately on the surface. The rotation was at the rate of forty revolutions per minute, a speed which gave ample stirring and yet was not violent enough to produce fine particles which would give the solubility an uncertain value. It is well known that the solution tension of a fine powder presenting sharply curved surfaces has a higher value than the flat surface of the same substance.[1]

In due time the rotation was stopped. The upper part of the test tube was brought to the surface of the bath by raising the whole rotating apparatus, and the wire and protecting rubber tube were carefully removed. The stopper was then withdrawn and two successive portions of the solution immediately removed by means of a filtering pipet, which consisted at first of an ordinary pipet with an attached rubber tube connecting successively extra tips loosely plugged with pledgets of cotton wool.[2] Before attaching the filtering device the pipet was provided with a large rubber stopper which closed the test tube when the pipet was lowered into it. A notch in this stopper providing inlet for air to displace the solution with drawn from the test tube. The pipet was kept at a proper temperature by enclosing it is a dry receptacle or sheath immersed in the thermostat. This method of removing the solution would, of course, need to be modified for use with higher temperatures, when evaporation would otherwise vitiate the results; but no trouble from this source seems to have arisen in our experiments, judging from the usual identity of analyses A and B, taken out one after the other from the same receptacle.

After withdrawing each portion of the solution from the test tube,

[1] P. Curie, *Bull. soc. chim.*, **8**, 145 (1885); see also G. A. Hulett, *Z. physik. Chem.*, **37**, 385 (1901).

[2] Richards and Fraprie, *Proc. Am. Acad. Arts Sci.*, **36**, 510 (1901). The pledgets of cotton were very small, hence the effect of adsorption must have been negligible. Comparison of results involving different bulks of solution, and those with the different forms of pipet, confirms this conclusion.

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the filtering attachment was quickly removed and (in the earlier determinations) the solution was run into a weighing bottle, which was immediately stoppered and weighed. Later it was found to be more convenient to provide the pipet with a stopcock and to weigh the solution in the pipet itself, from which the liquid could be run directly into the platinum vessel used for evaporation. Samples withdrawn by each of these methods gave the same value (within the limit of error) for the solubility in the series (that at 25°) where both were used. Expts. 1 to 6, inclusive, were withdrawn by the first method; Expt. 7 by the second.

The solutions were evaporated to complete dryness in platinum basins on a steam bath duly protected from contamination by large watch glasses secured about 6 cm. above them. The residue was cautiously heated over a Bunsen flame, at first turned very low but gradually increasing in an hour to full intensity, while the platinum basins were kept closely covered by means of small, thin watch glasses. Such gradual heating causes but very little, it any, decrepitation. Only once was a determination lost from this cause—in this case it had been heated too quickly. If a few minute particles of the sulfate are found clinging to the watch glass they may be easily returned to the dish. The total residue was then fused at a barely adequate red heat, just above 884°, to constant weight, which was usually attained at once.

The weighings were made after complete cooling, by substitution against a suitable counterpoise. In the case of the solutions the counterpoise was either a weighing bottle or a weight pipet, respectively, similar to the ones used with the solution; in the case of the platinum dishes the counterpoise consisted of equal weights of other platinum vessels. The weights were standardized carefully by the usual method.[1] All the weighings were corrected to the vacuum standard, assuming the density of sodium sulfate to be 2.698°,[2] and driving the densities of the solution by interpolation from the data given by Lord Berkeley.[3]

The Definiteness of the Equilibrium.

Theoretically, such an equilibrium as that between sodium sulfate dekahydrate and its aqueous solution must be perfectly definite, but in practice some systems approach equilibrium so slowly that their use would be precluded. Unless a definite equilibrium is promptly attained, the whole attempt would be in vain. Therefore, the time of digestion was varied over wide limits, and it was found that equilibrium was very quickly established, as is easily seen in the tables of results given here-

[1] T. W. Richards, THIS JOURNAL, **22**, 144 (1900).

[2] Richards and Hoover, *Ibid.*, **37**, 111 (1915).

[3] Earl of Berkeley, *Phil. Trans.*, (*A*) **203**, 209 (1904). For solutions saturated at 15.65°, 20.35°, 24.90°, the densities were found by him to be 1.115, 1.155 and 1.207, respectively.

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with. Even at 15°, where the attainment of equilibrium is naturally slower than that at higher temperatures, one-half hour's agitation in the apparatus (No. 18) served to give almost precisely the same degree of saturation as two hours (No. 16), and in other trials even five or six hours produced no further effect. Moreover, the equilibrium was approached from both sides, in order to be sure that no accidental errors existed. Measurements in which the system was brought from a lower temperature to that of the thermostat (Nos. 1, 3, 5, 8, 9, 10, 11, 13, 14, 16, 18) agreed with corresponding measurements in which the system was brought from a higher point to this same temperature (Nos. 2, 6, 9, 7, 12, 15, 17). No. 19 was made after all the others, in order to be sure that the early values near 25° could be repeated. Evidently, then, this system is excellently adapted to serve the purpose for which it was chosen; it combines all the necessary qualities in adequate fashion.

Tests were made to see if the glass test tubes were appreciably soluble in solutions of sodium sulfate. Two test tubes containing sodium sulfate solution and an excess of crystals were rotated at a temperature of 24° for a period of two hours. One was a test tube which had been used in several solubility experiments, and the other a new tube, which had been thoroughly cleaned in a manner similar to that used in the actual experiments. The tubes were weighed against a similar counterpoise before and after the rotation. Test tube I gained 0.05 mg. and test tube II showed no appreciable change in weight. Clearly the solubility of the glass was too slight (at these temperatures and in these comparatively short times) to affect the result.

Ascertaining the Temperatures.

An accurate Beckmann thermometer (more convenient than the standard thermometers for the measurement of small fluctuations) indicated the temperature of the thermostat, and this thermometer was then compared with the standard Baudin thermometers Nos. 1527 and 1520. The latter were read (by means of an accurate Geneva cathetometer) many times from both sides in order to avoid any errors which might be due to irregularities in the glass. The mean of all readings was taken as the uncorrected reading for that temperature. The ice points were determined in the usual way and all the precautions mentioned by Guillaume[1] were observed. A typical example of the full data of a single determination is given below. It will be observed that special heed was given to the effect of pressure on the thermometers.

This value (14.733°) is the hydrogen scale reading corresponding to 0.290° on the Beckmann under 740 mm. pressure. Hence with the corrected barometer at 746 and Beckmann at 0.290 the reading

[1] Guillaume, "Traite de la Thermometrie," 1889.

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would have been 14.732°, since the effect of 10 mm. pressure on the Beckmann bulb was 0.002°. 14.732° was therefore taken as the true temperature at the time of solubility Expt. No. 18.

TABLE II.

Full Data of Determination 18.

Barometer 746 mm., Beckmann 0.290°.

	Analysis A.		Analysis B.
Wt. of solution	41.0384		21.8057
Vacuum correction (density of solution 1.107)	+0.0385		+0.0204
Corrected wt. of solution	41.0769		21.8261
Wt. of Na_2SO_4	4.7002		2.4973
Vacuum correction (density 2.698)	+0.0015		+0.0008
Corrected wt. of Na_2SO_4	4.7017		2.4981
Wt. of H_2O	36.3752		19.3280
G. Na_2SO_4 per 100 H_2O	12.926		12.925
Determination of Temperature. Barometer 740 mm., Beckmann 0.290°.			
Baudin thermometer No.	15.276		15.200
Observed reading	14.968		15.001
Corr. for calibration	—0.043		—0.009
Corr. for exterior pressure	+0.002		+0.002
Corr. for interior pressure	+0.033		+0.023
Corr. for fundamental interval	+0.001		+0.010
Corr. for similarly corrected ice point	—0.160		—0.222
	14.801		14.805
Corr. to hydrogen scale	—0.070		—0.070
Final values[1]	14.731		14.735
Mean value		14.733°	

The following table (Table III) contains the results, the temperature and solubilities being ascertained in precisely the manner indicated in Table II. All of the results obtained are given in the following table, excepting determination 4, in which the thermostat was so inconstant as to make the result meaningless, and Analysis B of determination 2, which was invalidated by known loss from explosive decrepitation. In Nos. 5, 7, 12 and 15 only one analysis was made. The last column gives the individual values corrected to the exact temperatures designated as pertaining to the average in each case. The correction to be applied to the mean values given in the next to the last column is easily found in each case from the solubility curve. For each 0.001° it amounts at 25° to 2.0 mg.; at 22.5°, 1.7 mg.; at 20°, 1.4 mg.; at 17.5°, 1.2 mg.; and at 15°, 1.0 mg.

[1] The difference between the corrected Baudin thermometers was rarely as great as in this case. Usually they agreed with one another within 0.002°.

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TABLE III.

Determination at 25°.

Concentration of solution, g. salt per 100 g. water.

No.	Time.	Temperature. (Hydrogen scale.)	Analysis A. G.	Analysis B. G.	Mean. G.	Corrected mean. G.
1	3 hrs.	24.845°	27.468	27.468	27.468	27.468
2	6 hrs.	24.845°	27.465	..	24.465	27.465
3	3 hrs.	24.849°	27.475	27.474	27.475	27.467
5	3 hrs.	24.847°	27.475	..	27.475	27.471
6	5 hrs.	24.847°	27.470	27.473	27.472	27.468
19	1 hr.	24.843°	27.463	27.460	27.462	27.466
		Solubility at 24.845° per 100 g. water: Mean, 27.468				
7	3 hrs.	22.265°	22.597	..	22.597	22.597
8	5 hrs.	22.265°	22.607	22.600	22.604	22.604
9	1 hr.	22.265°	22.602	22.602	22.602	22.602
		Solubility at 22.265° per 100 g. water: Mean, 22.601				
10	2 hrs.	19.857°	18.859	18.858	18.859	18.863
11	2 hrs.	19.861°	18.873	18.872	18.873	18.872
12	3 hrs.	19.860°	18.863	..	18.863	18.863
		Solubility at 19.860° per 100 g. water: Mean, 18.866				
13	2 hrs.	17.472°	15.805	15.805	15.805	15.805
14	3 hrs.	17.470°	15.807	15.804	15.806	15.808
15	2 hrs.	17.472°	15.807	..	15.807	15.807
		Solubility at 17.472 per 100 g. water: Mean, 15.807				
16	2 hrs.	14.732°	12.926	12.924	12.925	12.924
17	1 hr.	14.731°	12.925	12.924	12.925	12.925
18	1/2 hr.	14.732°	12.926	12.925	12.926	12.925
		Solubility at 14.731° per 100 g. water: Mean, 12.925				

Thus five results for the solubility of sodium sulfate covering a range of ten degrees are provided, and the problem remains to interpolate other values between them. This may, of course, be done approximately by means of a graph; but since this graph would have to be drawn on a very large scale in order to attain a degree of accuracy, equalling that of the analytical work, it seemed worth while to derive an equation fitting the points as nearly as possible. The known values for the solubilities at 14.731°, 19.860° and 20.845° were substituted in the equation

$$\text{Log S} = a + bt + ct^2. \qquad \text{(I)}^1$$

The three equations were solved simultaneously for a, b and c. The result follows:

$$\text{Log S} = 0.6600577 + 0.0296154t + 0.0000696191t^2 \qquad \text{(II)}$$

The solubilities for 17.472° and 22.265° were then computed and found to agree closely but not exactly with those found at these temperatures. The results are given in Table IV:

[1] Nordenskiold, *Ann. Phys.*, [2] 136, 309 (1869).

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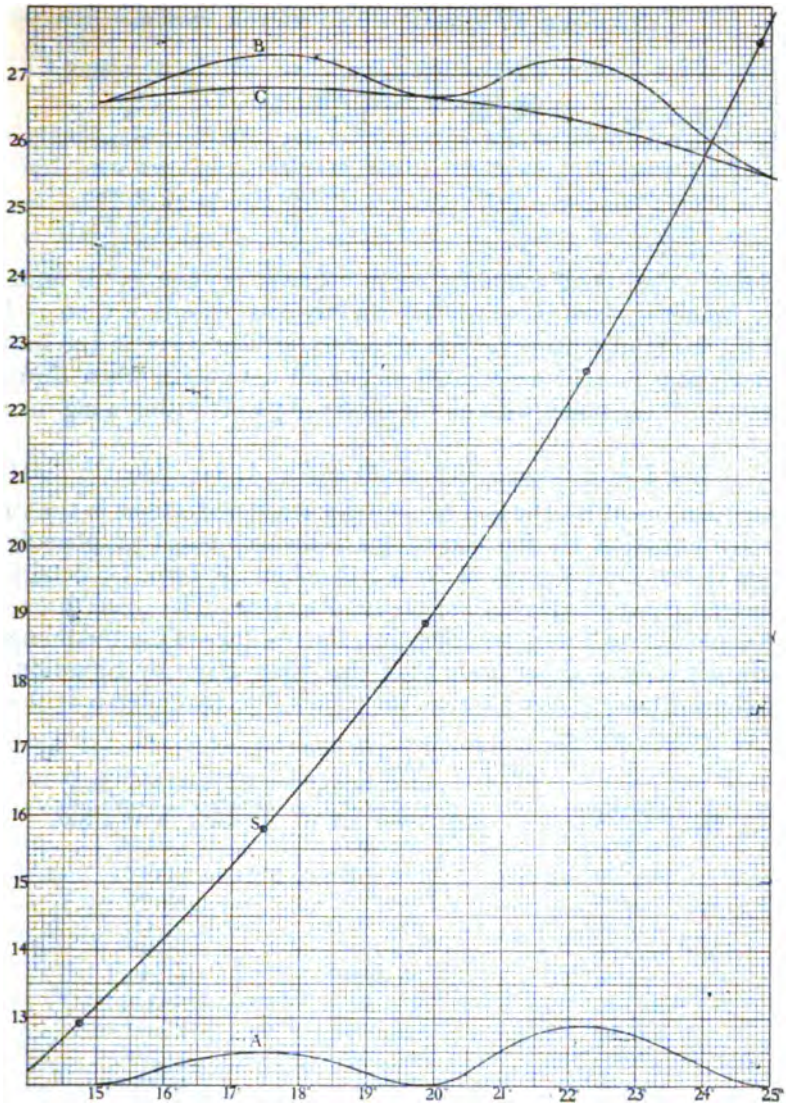

SOLUBILITY OF SODIUM SULFATE.

The diagonal curve (S) represents the solubility of sodium sulfate, grams of salt per 100 grams of water being plotted in the direction of ordinates, and degrees centigrade as abscissas. (The difference between the two standards of temperature is less than the thickness of this line as drawn.)

Curve A, the undulating deviation curve at the bottom, indicates (reading upward) the correction to be *added* to the value from Equation II at any given temperature in order to obtain the solubilities in terms of the Baudin hydrogen scale. Curve B, the undulating deviation curve at the top, similarly indicates (reading downward from the top of the diagram) the correction which must be *subtracted* from the value from Equation II in order to obtain the solubility in terms of the platinum scale of temperature (as indicated by Dr. H. N. Davis's platinum thermometers). Curve C, just below Curve B (also reading downward), records the number of milligrams to be *subtracted* from each solubility as recorded in Table V, in order to reduce the data to the platinum scale. In the case of the three deviation curves, the scale is magnified 100 times; each small square in the direction of ordinates indicates 1 mg.

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TABLE IV.

Temperature.	Solubility. Found.	Solubility calc. Equation II.	Δ.
14.731	12.925	12.925	0.000
17.472	15.807	15.802	—0.005
19.860	18.866	18.866	0.000
22.265	22.601	22.592	—0.009
24.845	27.468	27.468	0.000

Evidently the actual solubility curve between 15° and 25° is made up of two branches, each of which has slightly less curvature than is indicated by the total tendency, with a slightly greater curve in the middle. The deviations may be distributed among all the points, when Equation III results. This agrees with all the observed points within 4 mg. in each case.

$$\text{Log } S = 0.659970 + 0.02963889t + 0.0000688925t^2. \quad \text{(III)}$$

A better agreement is to be had by applying small corrections to the values given by Equation II, the corrections being computed graphically by plotting the deviations given in the fourth column of Table IV, depicted in the sinuous curve at the bottom of the diagram. The corrections thus found could hardly be less accurate than the readings of the thermometer, and are probably more accurate than the values given by Equation III. The following table (Table V) gives the results thus computed for the solubility of sodium sulfate.

TABLE V.

Temperature. Paris hydrogen scale.	Correction to be added to Eq. Calc. value. Eq. II.	Corrected calc. value. Solubility of $Na_2SO_4 10H_2O$. G. Na_2SO_4 in 100 g. H_2O.
15.000°	±0.000	13.181
16.000°	+0.003	14.185
17.000°	+0.005	15.268
18.000°	+0.005	16.437
19.000°	+0.002	17.698
20.000°	±0.000	19.064
21.000°	+0.005	20.549
22.000°	+0.009	22.155
23.000°	+0.008	23.888
24.000°	+0.003	25.762
25.000°	±0.000	27.795

These results are plotted in the accompanying graphs (diagrams). The values agree closely with Loewel's at 15° and Lord Berkeley's at 24.90°, but show marked deviations from some of the other old data.[1]

[1] Professor H. G. Deming has very kindly interpolated our experimental figures according to a different equation and one of his ingenious graphical methods. At only three of the eleven temperatures recorded above did his results differ over 3 mg. from the values given above, his method giving results decidedly closer to the experimental values than did the uncorrected Equation II. This outcome gives one confidence that the interpolation above recorded is very close to the truth. (See H. G. Deming, THIS JOURNAL, 39, 2137 (1917).) Lord Berkeley, in a kind letter just received, states that his records show his determination at 15.65° to have been not very reliable.

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The Comparison of the Baudin Thermometers with the Platinum Resistance Thermometer.

The Baudin thermometers upon which the foregoing table rests were also compared with two platinum resistance thermometers, in the Jefferson Physical Laboratory of Harvard University, with the kind help of H. N. Davis. The platinum thermometers were carefully standardized against ice, steam and the boiling point of sulfur. Great care was taken in this work, and it involved much time and labor. During the comparison the thermometers were immersed in a closed, cylindrical vessel, properly stirred, which in turn was placed wholly beneath the water of a thermostat. The details will be given in another place. The outcome was not very satisfactory: the five temperatures given in Table IV were found to be, respectively, 0.015, 0.010, 0.009, 0.010 and 0.012° higher as read by the platinum thermometer than as read by the Baudin thermometers. The platinum thermometers agreed with one another, but so also did the mercury thermometers, and the outcome points to an uncertainty of the thermometric scale in the neighborhood of 20°, amounting to about 0.01°. On applying these corrections a new series would, of course, be obtained to take the place of Table V, the weight of dissolved salt being, roughly speaking, 0.07% less in each case, with some variation. We find ourselves unable to decide between these two thermometer scales. Those who prefer the platinum scale can easily compute from the data given the exact values of the corresponding figures. The uncertain part of the work is not the analytical determination, but rather the knowledge of the temperature. It is easy to measure the solubility as accurately as necessary.

Even as it is, the values given in Table V make possible the standardization of thermometers within 0.01°, which is about the limit of accuracy of reading the graph depicting the results. For this reason, in spite of the uncertainty, it seemed worth while to publish the results, especially because they are more complete than any which have yet been published on this subject, and because they exemplify a method which may, in the future, become really valuable and convenient, especially for the calibration of Beckmann thermometers. The present paper is to be looked upon merely as preliminary and subject to future revision when the normal state of the world has been restored.

We are indebted to the Carnegie Institution of Washington for some of the apparatus employed.

Summary.

The solubility of sodium sulfate may be conveniently used in determining temperatures between 15° and 25° because:

(*a*) The salt changes its solubility greatly with changing temperature;

(*b*) It is easily obtained pure;

(*c*) It attains the saturation point quickly from either direction;

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(*d*) The solubility is easily determined with accuracy.

Preliminary determinations of the solubility of the dekahydrate of sodium sulfate have been made at about 15°, 17.5°, 20° and 25°, referred to the Paris hydrogen scale through standard Baudin thermometers.

Adequate constants for a usual empirical equation have been derived connecting temperature and solubility over this range, and the values at degree intervals have been computed.

The Baudin scale as given by these two thermometers does not exactly correspond with the platinum scale in this region. For the present we cannot explain the divergence, which diminishes the certainty of the results, but does not entirely destroy their usefulness.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY.]

THE ELECTROLYSIS OF SOLUTIONS OF THE RARE EARTHS. III.[1]

BY L. M. DENNIS AND A. B. RAY.

Received November 12, 1917.

I. Electrolysis of Neutral Solutions of the Nitrates of the Rare Earths.

In a previous article upon this subject,[1] the fractional precipitation and separation of the rare earths by the electrolysis of aqueous solutions of their salts at voltages considerably higher than the decomposition values of these compounds were explained as probably due to the action of the hydroxyl ions, concentrated near the cathode, upon earths of different basicities, the hydroxide of the weakest base being precipitated first. If this explanation is correct, it follows that the selective precipitation of the hydroxides in the order of the basicities of the earths should proceed more evenly, and the separation of the earths be more complete, as the vigor with which the electrolyte is stirred is increased, because this would bring the hydroxyl ions more frequently into contact with the weakest bases and would thus tend to lessen the simultaneous precipitation of hydroxides of earths of different basicity.

With a view to gaining experimental evidence upon this point, two portions of a solution of certain rare earths were electrolyzed under identical conditions except that one solution was vigorously stirred, whereas the other was agitated just rapidly enough to keep the surface of the mercury cathode free from adherent deposit of the precipitated hydroxides.[3]

[1] This article is a summary of a portion of the thesis presented to the Faculty of the Graduate School of Cornell University by A. B. Ray in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Dennis and van der Meulen, THIS JOURNAL, 37, 1963 (1915).

[3] For detailed description of the apparatus that was used for the electrolysis see Dennis and van der Meulen, *Loc. cit.*

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The mixture of rare earths that was employed contained the yttrium and erbium groups and a trace of neodymium, but was free from thorium, cerium and the more common elements. The average atomic weight of the earths in the mixture was 106.95. A neutral solution of the nitrates of these earths was prepared and was diluted with water until it contained 34 g. of oxides to the liter. Two portions of this solution, of five liters each, were used for the electrolyses. The containers for the solutions were glass cylinders about 20 cm. in diameter. A layer of mercury about 1.5 cm. deep, which served as cathode, was placed in each cylinder, and this was covered with five liters of the solution of the earths. A porous cup 6 cm. in diameter and 15 cm. deep was suspended in the electrolyte and was filled to within one cm. of the height of the outer solution with a 10% solution of nitric acid. The concentration of the acid in the cup was kept approximately constant during the electrolysis by fitting the cup with a constant-level siphon, and slowly dropping distilled water into the cup during the run. Agitation of the mercury cathode and of the solution was effected by air blown through glass tubes that dipped below the surface of the mercury. One cell was provided with two such air jets, the other with twelve. A sheet of platinum, inserted in the porous cup, served as anode.

The electrolysis was begun immediately after the porous cups were put in place and the anodes inserted. A current of three amperes was used and the electrolysis was continued until the amount of the hydroxides desired for the fraction had been precipitated.

The hydroxides precipitated in the two cells were distinctly different in character. Where the stirring had been slight, the hydroxides were granular and were easily collected on a filter. The precipitate in the cell in which the stirring had been vigorous was very finely divided and could rapidly be separated from the liquid only by filtration through a pad of macerated filter paper with the aid of suction. Moreover, the precipitated hydroxides from this second cell were dark in color because of the presence of finely divided mercury. We observed no indication of the formation of an amalgam of the rare earths, thus confirming the statement of Kettembeil.[1]

When an amount of the rare earth hydroxides desired for one fraction had been precipitated, the current and air blast were turned off, and the porous cups were removed from the cells. The solution in each cell was siphoned off and was then filtered on a Büchner funnel to remove the suspended hydroxides. The mercury and the hydroxides still remaining in the cell were transferred to a separatory funnel, the mercury was drawn off, and the hydroxides were then brought upon the filter. The precipitate was thoroughly washed with water and was then treated with

[1] *Z. anorg. Chem.*, 38, 213 (1904).

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warm 2 *N* hydrochloric acid which quickly dissolved the hydroxides but left most of the finely divided mercury undissolved. Hydrogen sulfide was passed through the filtrate to remove the slight amount of mercury that had been dissolved, the solution was again filtered, the hydrogen sulfide was removed by boiling, and the rare earths were precipitated by oxalic acid. The oxalates were washed with hot water until free from chlorides and were then dried at 100°.

The residual solution from which the precipitated hydroxide has thus been removed, together with the wash water which had been evaporated to small bulk, were returned to the cell and the electrolysis was continued until a second fraction of the rare earth hydroxides had been precipitated. This precipitate was removed and purified as before, and electrolysis was repeated until nine fractions had been obtained. The rare earths still remaining in solution were then precipitated by oxalic acid.

The atomic weight of each fraction was determined by the oxalate-oxide method. The absorption spectrum of each fraction was studied with the aid of a Krüss spectroscope, and the relative intensities of distinctive bands were approximated by the method of Dennis and Bennett.[1] A neutral solution of the chlorides of the earths, containing 5 g. of the oxides in 25 cc., was employed in each spectroscopic examination.

The data obtained in these two series of electrolyses are given in Tables I and II.

TABLE I.

Cathode area—452.4 sq. cm.

Atomic weight of original mixture—106.95.

Catholyte stirred vigorously by means of 12 air jets.

Number of fraction.	Atomic weight.	Weight of oxides (g.).	Ampere hours.	Volts.
1	121.84	19	34.5	7
2	114.80	18.68	27	7
3	112.24	22.16	27	7
4	108.77	17.12	22	7.4
5	105.85	14.42	22	7.6
6	103.15	10.06	18.5	8
7	100.82	12.32	19	9
8	97.58	11.80	22	11
9	94.68	14.50	22	15
10	95.58	2.02	Pptd. by oxalic acid	

The atomic weights of the various fractions and the relative intensities of the distinctive absorption bands of the "colored" earths in the fractions are plotted in Plates I and II. The spacing of the fractions along the axis of abscissas is based upon the actual weights of the several fractions.

[1] THIS JOURNAL, 34, 7 (1912).

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TABLE II.

Cathode area—452.4 sq. cm.
Atomic weight of original mixture—106.95.
Catholyte slightly stirred by means of two air jets.

Number of fraction.	Atomic weight.	Weight of oxides (g.).	Ampere hours.	Volts.
1	119.61	25.56	34.5	7
2	112.27	25.20	27	7
3	111.42	19.44	27	7
4	105.85	23.30	22	7.4
5	105.22	17.94	22	7.8
6	101.21	13.56	18.5	8.2
7	100.20	13.26	19	9
8	97.10	13.98	22	11
9	96.00	10.36	22	15
10	98.20	1.54	Pptd. by oxalic acid	

Comparing the results of the two series of electrolyses it will be noted that as the vigor of stirring of the catholyte is increased there results a somewhat more rapid segregation of the earths of higher atomic weights in the first fractions and a better concentration of the earths of lowest atomic weight (chiefly yttrium) in the last fractions. Vigorous stirring also

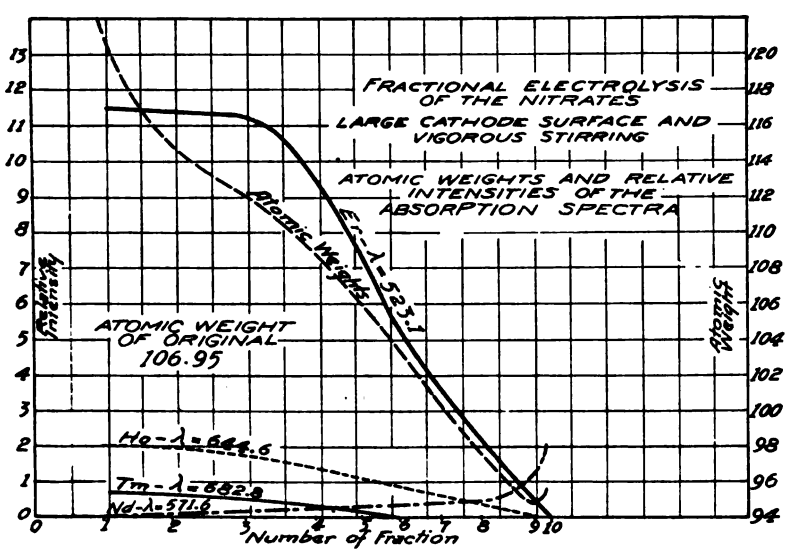

Plate I.

accelerates the precipitation of erbium, holmium and thulium, which results in a higher concentration of neodymium (and yttrium) in the last fractions. A third series of electrolyses in which the stirring was still more rapid showed further accentuation of the differences.

These results show, therefore, that when a neutral nitrate solution of the rare earths here indicated is fractionally electrolyzed with a dia-

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phragm in the manner described, the hydroxides of the earths are precipitated in the order of their basicities,[1] and their separation is the more complete the more vigorously the mercury cathode and the catholyte are stirred.

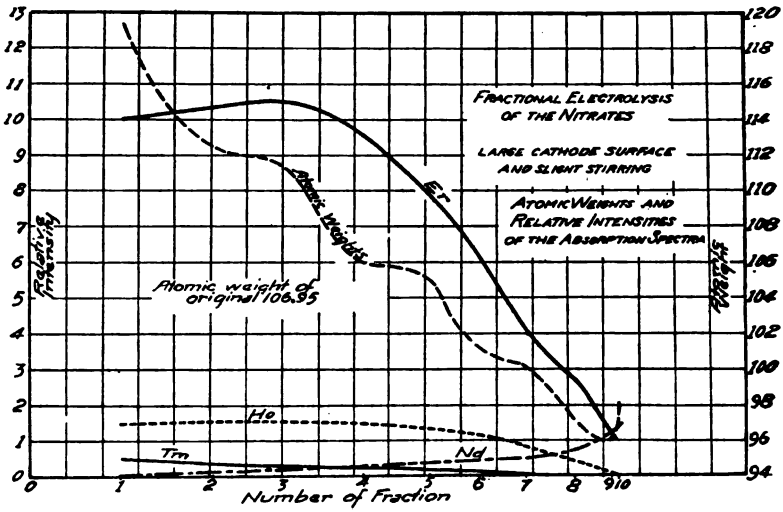

Plate II.

II. Electrolysis of Neutral Solutions of the Nitrates of the Rare Earths and Thorium Nitrate.

The weakly basic character of thorium seemed to render it probable that electrolysis of a solution containing thorium nitrate and nitrates of the rare earths might result in the rapid concentration of thorium in the early fractions. Thorium for commercial uses is now extracted on a large scale (about 300,000 kg. of thorium nitrate per annum) from monazite. For this reason the electrolytic separation of thorium from the earths with which it is associated in monazite, possessing as it does a practical interest, was investigated. The mixture of the rare earths was prepared from the by-product of the technical separation of thorium from monazite. This material was carefully purified and was freed from cerium and thorium. The earths were converted to the oxides, and from this mixture of the oxides a neutral solution of the nitrates was prepared. The concentration of the solution was then determined by precipitation with oxalic acid and ignition of the oxalate to oxide.

A clear, neutral solution of thorium nitrate was prepared by adding pure, moist thorium hydroxide to cold, dilute nitric acid until the hydroxide was in excess, and then allowing the material to stand until a test with Congo-red paper showed the absence of free acid. The solution

[1] R. J. Meyer, Abegg's "Handbuch der anorganischen Chemie," 3, 147.

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was then separated from the undissolved hydroxide, and its concentration was determined.

The electrolysis was conducted in the manner already described, very vigorous stirring of the catholyte and mercury cathode being employed.

(*a*) **Electrolysis of Solutions of Thorium Nitrate.**—Electrolyses of solutions of thorium nitrate alone were first made to ascertain whether the precipitation of the hydroxide may most satisfactorily be made from cool or from hot solution. The electrolyses were made in two cells, connected in series. The solution in one cell was kept at 22° during the run; that in the second cell at about 90°. A dilute solution of thorium nitrate (1.3 g. ThO_2 in 100 cc.) was placed in each cell. The electrolysis was conducted as before described, a current of two amperes being employed. The voltage across the cold cell rose from 6 volts at the beginning to 40 volts at the end of the run; that across the warm cell, from 5 volts to 30 volts. The current required for practically complete precipitation in the cold cell was 5 ampere hours; in the warm cell, 4.75 ampere hours. The current required by theory for complete precipitation was 4 ampere hours. This showed a current efficiency in the cold cell of 80%; in the warm cell, of 84.2%. The precipitate of thorium hydroxide in the cool cell was granular, was easily filtered and washed, and contained almost no finely divided mercury. The thorium hydroxide thrown down in the warm cell was flocculent, contained much finely divided mercury, and was filtered and washed with difficulty.

From these results it was apparent that the electrolysis of a solution of thorium nitrate operates most satisfactorily when conducted at about room temperature.

To determine the influence of the concentration of the electrolyte upon the character of the precipitate, three solutions of thorium nitrate containing 0.5%, 5%, and 20% of thorium dioxide, respectively, were electrolyzed in small cells of about 300 cc. capacity. The thorium hydroxide precipitated from the 20% solution in very finely divided form resembling a colloidal solution. The character of the precipitates in the other two cells showed that as the concentration of the solution is lowered (down to 0.5%) the granular form of the hydroxide becomes more pronounced. Because of these results, the later electrolyses of mixtures of thorium nitrate and the nitrates of the rare earths were made with solutions that contained about 0.5 g. thorium dioxide per 100 cc.

(*b*) **Electrolysis of Solutions Containing Thorium Nitrate and Nitrates of the Rare Earths.**—A solution containing, in 3.5 liters, 14.72 g. of thorium oxide and 85 g. of the oxides of the rare earths (av. at. wt. 140.5) was electrolyzed with a current of one ampere. The mercury cathode was vigorously stirred during the electrolysis, and the concentration of the

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acid in the porous cup was kept practically constant. At the end of six hours, the electrolysis was interrupted and the precipitated hydroxides were collected and purified in the manner already described. The hydroxides were then dissolved in 2 *N* nitric acid, an excess of acid being avoided. To this solution there was added one-fifth of its volume of a concentrated solution of ammonium nitrate,[1] the solution was then heated to from 60–80°, and an excess of 10% hydrogen peroxide was added. Thorium is thus quantitatively precipitated as the hydrated peroxide, the rare earths remaining in solution.[2] The precipitate was collected on a filter, thoroughly washed, and then dissolved in 2 *N* hydrochloric acid. The solution was diluted to one liter and 25 cc. portions were precipitated by ammonium hydroxide, and the thorium hydroxide ignited to the oxide, and weighed.

The filtrate from the first thorium precipitation by hydrogen peroxide was diluted to 500 cc., 25 cc. portions were precipitated by oxalic acid, and the oxalates of the rare earths were ignited to oxides and weighed.

The filtrate from the first fractional precipitate of the hydroxide, together with the wash water, were returned to the cell and electrolyzed as before. The procedure was again repeated, three fractional precipitations in all being made. The results are set forth in the following table:

TABLE III.

Volume of electrolyte, 3.5 liters. Total amount ThO_2 and R_2O_3 present in the solution = 99.72 g., of which ThO_2 = 14.72 g. (14.76%), R_2O_3 = 85.00 g. (85.24%). Average atomic weight of rare earths = 140.5. Current = one ampere.

Fraction number.	Ampere hours.	Wt. in g.		Per cent.	
		ThO_2.	R_2O_3.	ThO_2.	R_2O_3.
1	4	5.048	1.372	78.63	21.37
2	6	3.94	7.40	34.75	65.25
3	7	2.22	8.88	20.0	80.0

The results show that fractional electrolysis effects a marked concentration of thorium in the early fractions, from about 15% in the original mixture to over 78% in the first fraction, and nearly 35% in the second fraction.

Another electrolysis was run to determine to what degree thorium would be concentrated in the first fraction when it was associated with the monazite earths in approximately the ratio in which it occurs in that mineral. A neutral solution of the nitrates containing 5.95 g. of thorium oxide and 112.85 g. of the rare earth oxides (av. at. wt. = 140.5) was diluted to 6.25 liters and electrolyzed as before with a current of one ampere.

[1] Benz, *Z. angew. Chem.*, 15, 303 (1902).

[2] Meyer and Hauser, "Die Analyse der seltenen Erden und der Erdsäuren," pp. 250–251.

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TABLE IV.

Fraction number.	Ampere hours.	Wt. in g.		Per cent.	
		ThO_2.	R_2O_3.	ThO_2.	R_2O_3.
1	3	1.53	1.44	52	48

From these results it is seen that a single fractional electrolysis of three hours' duration precipitates nearly 26% of the thorium present and that the precipitated hydroxides contain 52% of ThO_2 as against 5% in the original mixture.

ITHACA, N. Y.

[CONTRIBUTION FROM THE LABORATORY OF INORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY.]

THE PRECIPITATION OF COLLOIDAL GOLD AND PLATINUM ON METALLIC SURFACES.

BY ELLWOOD B. SPEAR AND KENNETH D. KAHN.

Received November 6, 1917.

In this article we submit experimental evidence to show that when colloidal gold or platinum is precipitated by metallic surfaces the most active metals are the most effective, that is, the more electropositive the metal is toward the hydrogen electrode the shorter will be the time required for the complete precipitation of the colloid. The evidence also shows that some of the metal, of which the surface is composed dissolves, is adsorbed by the colloidal particles, and is consequently carried down with the colloid. The precipitation of the colloid by metallic plates is therefore quite analogous to that produced by the addition of an electrolyte.

Our attention was directed to this work through an article by M. Phillippson[1] in which he stated that colloidal silver is precipitated by zinc plates but not by plates of gold or platinum. Phillippson was unable to form any definite conclusions relative to the mechanism of the precipitation, although he surmised that the position of the precipitating agent in the electrode potential series was a vital factor. This we have shown to be correct. Phillippson also suggested that the relation of the activity of the precipitating metal to that of the colloidal metal might have a deciding influence. For example, because copper is more active than silver a plate of copper could precipitate colloidal silver, but a silver plate could not precipitate colloidal copper. From the results of our investigations there would seem to be no necessity for making such an assumption in order to explain the precipitation.

Preparation of the Colloidal Solutions.

The water used in the preparation of the colloidal solutions was that employed for conductivity purposes in the Research Laboratory of

[1] *Kolloid Z.*, 11, 49 (1912).

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Physical Chemistry of the Institute. The colloidal solutions of gold and platinum were prepared by Bredig's well-known method of electrical colloidation. No alkali was added while producing solutions of platinum, but because of its instability in pure water, colloidal gold was made in 0.001 N sodium hydroxide solutions.

All the vessels employed were carefully cleansed with chromate solutions, thoroughly washed with distilled water, rinsed with conductivity water and finally treated with steam from conductivity water. These precautions insure the stability of the colloidal solutions, some of which have been kept in the laboratory for over two years without any appreciable amount of precipitation taking place.

Experimental Method.

The first experimental work was designed to determine the relation of the precipitating effect of the metal and its position in the electrode potential series. To this end well-polished plates of zinc, steel, nickel, lead, tin, copper and platinum having approximately the same amount of exposed surface, were placed in a definite amount of the gold and platinum solutions. All conditions as to temperature, amount of surface of the liquid exposed to the air, etc., were kept as nearly as possible identical throughout each series. Table I gives a typical set of results for colloidal platinum, while Table II gives a similar set for colloidal gold.

TABLE I.—COLLOIDAL PLATINUM.

	Time in hours.			
Metal.	3/4.	1.	2.	72.
Zinc.....	part coag.	all coag.	....	....
Steel.....	....	part coag.	all coag.	....
Nickel.....	....	part coag.	all coag.	....
Lead.....	....	....	part coag.	....
Copper.....	....	....	....	all coag.
Platinum.....	....	....	....	....

TABLE II.—COLLOIDAL GOLD.

	Time in hours.			
Metal.	1.	4.	19.	49.
Zinc.....	part coag.	nearly all coag.	all coag.	....
Steel.....	slight amount coag.	part coag.	all coag.	....
Nickel.....	.....	....	all coag.	....
Tin.....	.....	....	part coag.	all coag.
Copper.....	.....	....	slight amount coag.	all coag.
Platinum.....	.....	....	.....	....

It is evident from the above results that the most reactive metals require the least time to coagulate the colloidal solutions and that inactive metals will not produce coagulation at all. It should be noted, however, that the condition of the surface is an important factor. For instance, it was found that slightly rough surfaces formed by the electrolytic de-

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position of the metal were more efficient than smooth plain surfaces. Thus a copper strip having a plain surface had no visible effect on a quantity of colloidal gold in 24 hours, while another portion of the same strip, the surface of which had been roughened by electroplating, caused complete precipitation in this time. The same accelerated effect of the electrolytic over the plain surface was noted in the case of nickel and also that of lead. Moreover, as one might anticipate, it was found that zinc dust would precipitate colloidal gold or platinum much more rapidly than the same weight of zinc in the plate form. In fact 2 g. of zinc dust gently shaken with 10 cc. of platinum solution caused complete precipitation in less than one minute.

From a consideration of these results it would seem that the cause of the precipitation is the dissolving of the metal to form the corresponding positively charged ion. The ion then neutralizes the negative charge on the particles and consequently the colloid coagulates.

If this theory is correct it should be possible to prevent a copper plate from precipitating the colloid by keeping out the air because copper does not dissolve in pure water. In fact copper will not even tarnish in water from which the oxygen has been driven by hydrogen. That oxygen is essential for the precipitation of the colloid by copper was shown in the following manner:

A test tube containing the colloidal platinum was fitted with a two-hole stopper, through which two glass tubes passed. One of the tubes reached to the bottom of the test tube and served to introduce purified hydrogen into the solution. The other tube allowed hydrogen and the air to escape. The gas was bubbled through the solution for one-half hour, at the end of which time a plate of copper was introduced. Hydrogen was again bubbled through for one hour after which the tube was closed by means of pinchcocks. Another portion of the same copper plate was put into the same amount of the colloidal solution and the container left open to the air. The colloid was coagulated in the open tube in one experiment in 44 hours and in another in 72 hours, while the copper plates in the atmosphere of hydrogen had not affected the colloid in six days. When the tubes containing the hydrogen were opened to the air the colloid was completely coagulated in less than three days. This shows quite clearly that the metal must dissolve before precipitation can take place.

We were also able to predict another result from a consideration of this theory. If the metal dissolves on the surface, forms the ion and the ion discharges the colloidal particles, then, reasoning from our knowledge of precipitation by electrolytes, some of the metal should be adsorbed and carried down by the precipitated colloid. After several unsuccessful

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attempts with lead and copper, due to the relatively small amounts of the colloid used, we were able to show that copper is carried down with colloidal platinum when the precipitation is achieved by means of copper wires. The determination was made as follows:

600 cc. of a concentrated solution of colloidal platinum were placed in a beaker of one-liter capacity. Copper wires of about 1.5 mm. diameter were heated and reduced with alcohol. All tarnished portions were cut off and discarded. The wires were weighed, placed in the solution and the latter stirred at frequent intervals. The precipitation was complete in 36 hours. The copper wires were tarnished and, as might be expected, had increased slightly in weight. The precipitate was filtered and thoroughly washed with conductivity water. Neither the filtrate nor the wash water gave the slightest coloration with hydrogen sulfide.

The precipitate was treated in a casserole with concentrated nitric acid, evaporated to a small volume, diluted with water and filtered. The filtrate which was slightly brown was evaporated to about 2 cc. in order to drive off the excess of acid. It was then diluted with 10 cc. distilled water and saturated with hydrogen sulfide. A very considerable precipitate was obtained showing that coagulated colloidal platinum is appreciably attacked by concentrated nitric acid. The precipitated sulfides were then treated with ammonium polysulfide, whereby most or all of the platinum sulfide dissolved. The filter paper was washed and boiled with 2 *N* nitric acid. After filtering, the liquid was evaporated to a small volume, diluted with water, neutralized with ammonia and acidified with acetic acid. Two cc. of a solution of potassium ferrocyanide were then added. The first drop gave an unmistakable copper reaction. After standing some hours a small pink precipitate settled to the bottom of the tube. These experiments prove beyond a doubt that copper dissolves and is carried down by the colloid.

Summary.

In this article we have shown that:

Metallic plates precipitate colloidal platinum and gold in the same order as the metals occur in the electrode potential series, the most active metal requiring the least time.

A roughened surface or a finely divided metal requires less time than the same metal if the surface is smooth.

The metal dissolves, is adsorbed and carried down by the colloid.

The precipitating effect of the metal may be explained on the same basis as that of electrolytes.

CAMBRIDGE, MASS.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF VERMONT.]

THE DETERMINATION OF POTASSIUM AND SODIUM AS CHLORIDES THROUGH USE OF THE REFRACTOMETER.

BY B. A. SHIPPY AND G. H. BURROWS.

Received July 16, 1917.

The method about to be described for the determination of potassium and sodium as chlorides, each in the presence of the other, depends upon the facts that the refractive indices of aqueous solutions of potassium and sodium chlorides vary linearly with their concentrations and that the values of the indices of sodium chloride solutions are higher than are those of the corresponding solutions of the potassium salt, the difference increasing with increase in salt concentration. These facts are exhibited in Fig. I, in which the values of Table I are plotted. The indices are those for the D line, and measured at 25°. The instrument used was the Pulfrich refractometer.

The materials used in all of the recorded measurements were prepared as follows: The ordinary laboratory-distilled water was redistilled once, care being taken to prevent passage of spray into the condenser, and the first third of the distillate was discarded. Preserved in a glass container, this water showed uniformly, at 20°, a refractive index of 1.33307.

The potassium chloride of highest commercial purity was once recrystallized, with centrifugal draining. The crystals were heated in a platinum dish to dull redness and preserved in a desiccator.

Table salt was the source of the sodium chloride used. This was twice precipitated from its concentrated aqueous solution through saturating the solution with hydrogen chloride, generated by heating concentrated, chemically pure, aqueous hydrochloric acid. The crystals were drained and the final crystals ignited and preserved as in the case of the potassium salt. Constancy of refractive index indicated that further purification of the salts was not necessary.

TABLE I.

Salt.	G. salt.	G. solution.	% salt.	Index.
KCl	0.0602	1.2042	5.00	1.33931
KCl	0.2770	2.7700	10.00	1.34643
KCl	0.4468	2.9786	15.00	1.35335
KCl	0.5632	2.8162	20.00	1.35992
NaCl	0.2126	4.2520	5.00	1.34172
NaCl	0.9454	9.4536	10.00	1.35021
NaCl	0.9768	6.5118	15.00	1.35893
NaCl	0.9308	4.6536	20.00	1.36829

In Table II are given refractive indices at 25° of solutions of mixtures of potassium and sodium chlorides. In each solution, the total salt concentration is 20%.

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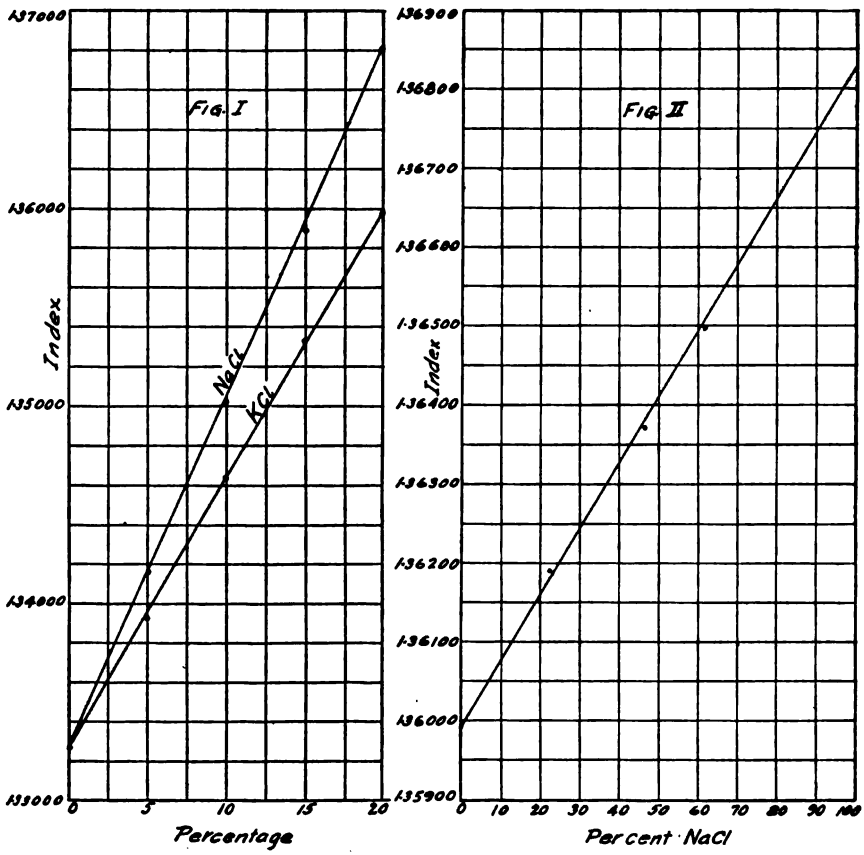
TABLE II.

Composition of salt mixture.		
% KCl.	% NaCl.	Index.
00.00	100.00	1.36829
39.20	61.80	1.36499
53.25	46.75	1.36372
67.67	22.23	1.36190
100.00	00.00	1.35992

The values of Table II are plotted as Fig. II. In this plot, the compositions of the salt mixtures dissolved are expressed in terms of their percentage contents of sodium chloride.



The determination is carried out as follows: From the salt mixture to be analyzed, consisting exclusively of potassium and sodium chlorides, a 20% solution is prepared as exactly as possible. This may be done with little expense of time by adding to the mixture, contained in a weighing bottle, slightly more than the calculated weight of water, and evaporating to just this weight, through passing a current of warm air over the

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surface of the solution. A single cc. of the solution is ample for the determination. The thoroughly mixed solution is brought to the temperature of 25° in the jacketed cell of the instrument and the index is determined. The necessity of precise control of the temperature is to be emphasized, since a variation of 0.1° in temperature changes the index about 0.00002. From the index of the mixture and those of the pure, single chlorides in 20% solution, the composition of the mixture is calculated by simple proportion. Thus the index of the 20% solution of a certain mixture was found to be 1.36244. The indices of the 20% potassium and sodium chloride solutions are, respectively, 1.35992 and 1.36829 (the first and last values of Table II), whence,

$$\frac{1.36829 - 1.36244}{1.36829 - 1.35992} = \frac{\% \text{ KCl}}{100}.$$

The total difference in refractive indices of 20% sodium chloride and 20% potassium chloride is only 0.00837. A change, then, of 1% in the relative concentration of a salt mixture will change the index only 0.00008, whereas a variation of 0.1% in total salt concentration changes the index about 0.00018. Because of these facts, and because of the marked variation of the index of refraction with variation of temperature, the method is not of high accuracy. Owing, however, to its comparative rapidity and to its avoidance of costly reagents, there may be instances in which it will prove of use.

Table III gives the results of several trial analyses.

TABLE III.

Actual composition (% KCl).	Index.	Composition calculated from index (% KCl).
69.44	1.36244	69.3
43.09	1.36463	43.7
28.95	1.36582	29.0
00.42	1.36820	1.1

BURLINGTON, VERMONT.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CINCINNATI.]

A NEW METHOD FOR THE SEPARATION OF THE COPPER GROUP FROM THE ARSENIC GROUP, WITH ESPECIAL REFERENCE TO THE IDENTIFICATION OF ARSENIC.

BY M. CANNON SNEED.

Received October 25, 1917.

In qualitative chemical analysis, yellow ammonium sulfide is universally employed for the separation of the copper from the arsenic group. This method is not entirely satisfactory, because some copper sulfide dissolves as well as the sulfides of arsenic, antimony, and tin.[1] To obviate

[1] Rössing, *Z. anorg. allgem. Chem.*, **25**, 407 (1900); *Z. anal. Chem.*, **41**, 1 (1902); Noyes, THIS JOURNAL, **29**, 170 (1907).

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this difficulty, Welsh and Weber[1] recommend the use of a solution of ammonium polysulfide containing about 5% of sodium hydroxide. Mercuric sulfide, however, is quite soluble in sodium sulfide,[2] which must be present in their reagent.[3]

Furthermore, the methods of qualitative analysis usually employed to separate the copper and arsenic groups lead the analyst into many difficulties. Colloidal suspensions interfere, free sulfur increases the complexities, the use of yellow ammonium sulfide is undesirable, and the whole procedure is not clean-cut, so that, unquestionably, much improvement is needed at this particular point in the scheme of analysis of the cations. This paper is written with a view of presenting a more desirable method of analysis for these two groups.

Procedure.

After mercurous mercury, silver, and lead have been removed by the addition of hydrochloric acid in the usual way, heat the filtrate to 90°, and saturate it with hydrogen sulfide by means of a *rapid* stream of the gas passed long enough to insure the complete precipitation of arsenic.[4] Without removing any precipitate which may form, add a volume of water equal to that of the solution, and again pass hydrogen sulfide. In case an excess of acid is still present,[5] filter the solution and evaporate the filtrate to dryness. Dissolve the residue in a solution prepared by adding 3 or 4 cc. of dilute hydrochloric acid to 75 or 100 cc. of water. Treat the resulting solution with hydrogen sulfide, and if any precipitate is produced, collect it on a filter, together with the previous one, and wash the combined precipitates with hydrogen sulfide water containing about 2% of ammonium nitrate.[6]

Prepare a special reagent as follows: Saturate a 12% solution of sodium hydroxide with hydrogen sulfide. Add to each liter of this solution 400 cc. of a 40% solution of sodium hydroxide.[7] Digest the combined precipitates of the copper and arsenic groups with this reagent. Mercuric, arsenous, arsenic, antimonous, antimonic, stannous and stannic sulfides dissolve, while lead, bismuth, copper and cadmium sulfides settle quickly, leaving above them a clear, almost colorless liquid, which is

[1] This Journal, 38, 1011 (1916).

[2] Gmelin-Kraut, "Handbuch d. anorg. Chem.," Ed. 7, 5, 1059 (1909).

[3] An appreciable quantity of HgS dissolves in ammon. polysulfide. It has been shown by Volhard, *Ann.*, 255, 255 (1889), that the presence of ammonium salts renders mercuric sulfide less soluble in the sulfide of sodium.

[4] Foster, This Journal, 38, 52 (1916).

[5] Stieglitz, "Qualitative Analysis, Laboratory Manual," 1916, p. 31.

[6] The use of the ammonium nitrate solution is recommended to prevent, as far as possible, any of the sulfides of these two groups from going into the colloidal condition, and thus reduce the likelihood of error in the analysis.

[7] Do not use sodium polysulfide.

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easily filtered.[1] Wash the residue thoroughly with hydrogen sulfide water, and dissolve it in the smallest possible amount of boiling, dilute[2] nitric acid. Probably a little free sulfur will remain. To the acid solution add two or three drops of dilute sulfuric acid, and evaporate it almost to dryness. Cool and treat the residue with water and a little dilute sulfuric acid. Collect any solid material on a filter paper and test it for lead, if lead has not been found previously; otherwise, it is discarded.[3] The filtrate may be tested for bismuth, copper and cadmium according to any standard scheme of analysis.

To the filtrate which contains the arsenic group, add sufficient ammonium carbonate[4] to precipitate the mercury completely.[5] When this precipitate is boiled with dilute hydrochloric acid containing a few crystals of potassium chlorate, it dissolves. Confirm the presence of mercury by adding this solution, which has been boiled to remove chlorine, to one of stannous chloride. Treat the solution, from which mercury was removed, with enough dilute hydrochloric acid to precipitate entirely the sulfides of arsenic, antimony and tin.[6] Collect the precipitate, and treat it with 10 to 20 cc. of concentrated hydrochloric acid; then warm the mixture until the vigorous evolution of hydrogen sulfide ceases. The

[1] Stannous sulfide dissolves rather slowly in the special reagent even at a temperature of 90°. If the solution be boiled, a part of the tin separates in the metallic form while the remainder is oxidized to the stannic condition: $2Sn^{++} \longrightarrow Sn + Sn^{++++}$. It is, therefore, advisable to digest the combined precipitates of the copper and arsenic groups for five to ten minutes at a temperature of 100° with the sodium sulfide reagent, in which it dissolves (Gmelin-Kraut, *Handbuch d. anorg. Chem.*, Ed. 7, 4, 289 (1911)):

$$Sn + 2NaOH + H_2O \longrightarrow Na_2SnO_3 + H_2$$

Unless stannous tin is present, the precipitates need be digested only two or three minutes. The prolonged treatment required to dissolve SnS may be avoided by boiling the solution, after the removal of the silver group, with sufficient nitric acid to oxidize the tin. The amount of acid required for this purpose is usually very small. After the oxidation is complete, the copper and arsenic groups should be precipitated with H_2S in the usual way. Stannous tin is not commonly met with in mixtures prepared for analysis.

[2] Dilute nitric acid, 6 *N*. Dilute hydrochloric acid, 6 *N*. Dilute sulfuric acid, 6 *N*.

[3] Sometimes basic bismuth sulphate is present in this residue.

[4] If trivalent antimony is present, add enough sulfur to change it to the pentavalent condition before ammonium carbonate is used, otherwise some antimonous sulfide will be precipitated.

[5] Volhard, *Loc. cit.*

[6] Another method for separating mercury from arsenic, antimony and tin is as follows: Mercuric sulfide may be precipitated by dilute HCl together with the sulfides of arsenic, antimony, and tin. When these sulfides are treated with concentrated HCl, mercuric sulfide remains undissolved with the sulfides of arsenic. HgS may be separated from As_2S_3 and As_2S_5 by dissolving the latter in concentrated ammonium hydroxide.

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sulfides of antimony and tin dissolve, while those of arsenic do not. Tin and antimony may be identified by various standard methods. Treat the residue, which consists of the sulfides of arsenic, and free sulfur, with 5 or 6 cc. of concentrated ammonium hydroxide. Arsenic, in either the tri- or pentavalent state, dissolves readily, leaving a residue of sulfur. First, neutralize the solution with concentrated nitric acid. If a yellow precipitate results, the presence of arsenic is indicated. Without filtering, treat the mixture with a moderate excess of concentrated nitric acid and boil it until a clear liquid results. Treat the hot solution, in a test tube, with an excess of ammonium molybdate.[1] Allow the contents of the tube to stand for several minutes at a temperature of 85 to 90°. If a large quantity of arsenic is present, an immediate yellow precipitate forms; but if there is only a trace of arsenic, half an hour may be required to obtain conclusive evidence of it. By this method, arsenic at a dilution of one part of 225,000 parts of water may be identified by using only 50 cc. of such a solution.

Discussion of the Method.

The method outlined has been used by classes in qualitative analysis with excellent results. They find that the separation of the copper from the arsenic group is precise, and that the identification of the individual ions is usually more conclusive by this than by other schemes. Students, in less than 5% of the cases, have failed to find arsenic, when present, or reported it when their unknowns contained no arsenic. This is exceptional, taking into consideration the fact that by following other methods an error of about 20% is recorded.[2]

By the transference of mercury from the copper group to the arsenic group two equal divisions containing four metals each[3] are obtained, with the further advantage of eliminating the uncertainty of separating completely the sulfides of lead, bismuth, copper and cadmium from mercuric sulfide when solution in nitric acid is depended upon for the separation. Grouping mercury with arsenic does not decrease the ease with which the Hg^{++} is identified.

For many reasons, the use of a mixture of sodium sulfide and sodium hydroxide as a reagent for the group separation, is a decided improvement over yellow ammonium sulfide. It is noteworthy, for example, that all the sulfides which are soluble in ammonium polysulfide, with the exception of copper sulfide, dissolve more readily in the sodium sulfide mixture. Again, as previously noted, the new reagent, unlike yellow ammonium sulfide, effects a complete separation of the groups, and at the same time leaves a solution from which the sulfides of lead, bismuth,

[1] A large excess of ammonium molybdate is necessary.

[2] Welsh and Weber, *Loc. cit.*

[3] Gold, platinum and molybdenum omitted.

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copper and cadmium separate as a dense residue with a clear, almost colorless, supernatant liquid, free from these sulfides, either suspended or dissolved. Furthermore, it is noted that cadmium sulfide, obtained as a final test for the Cd^{++}, is always of a pure yellow color, and not admixed with any other sulfide.[1] Finally, from a study of the chemical behavior of gold, platinum, and molybdenum it would be expected that the sulfides of these metals would be more readily soluble in a mixture of sodium hydroxide and sodium sulfide than in ammonium polysulfide.

To effect a separation of the copper and arsenic groups Prescott and Johnson[2] recommend the use of sodium sulfide, if mercury be absent, and state that ammonium polysulfide must be employed if tin be present in the stannous condition. But if mercury be transferred to the arsenic group, sodium sulfide must be used. Moreover, mercuric sulfide is more readily soluble in a mixture of sodium sulfide and sodium hydroxide than in sodium sulfide alone; and stannous sulfide dissolves completely in the *mixture* while it often fails to do so in yellow ammonium sulfide.[3] Probably this fact is to be explained by assuming that some salt, *e. g.*, Na_2SnOS, which may be formed under these conditions, possesses a low instability constant which accounts for the suppression of the Sn^{++}, and, therefore, greatly increases the solubility of stannous sulfide. It is true that stannites are much more stable than thiostannites.

Identification of arsenic, as ammonium arsenomolybdate, is readily made by dissolving its sulfides in concentrated ammonium hydroxide, thus freeing it from any sulfur which may be present. The arsenic is then confirmed according to the scheme. This procedure is much more desirable than to dissolve in nitric acid the sulfides of arsenic, together with a large amount of admixed sulfur, which is always present when ammonium polysulfide is used as a reagent. The use of ammonium hydroxide to effect a solution, and the subsequent use of nitric acid to precipitate the sulfides of arsenic and to redissolve them, gives a mixture containing ammonium nitrate and nitric acid, in the presence of which the molybdate test is most sensitive. This method for identifying arsenic is offered as a convenient and reliable wet test, when arsenic is present in concentrations not less than one part of arsenic to 225,000 parts of water, and when at such a dilution the analyst has at least 50 cc. of solution.

CINCINNATI, OHIO.

[1] Lead, which is frequently carried through to the point where Cd^{++} is determined, masks the color of cadmium sulfide. This complication arises from the use of too much sulfuric acid or too concentrated nitric acid, both of which dissolve an appreciable amount of lead sulfate. This sulfate, in such acid solutions, is not reprecipitated by ammonium hydroxide, which is employed to precipitate $Bi(OH)_3$, because lead sulfate is soluble in ammonium salts, which makes it possible for lead to be carried over to the point where cadmium is detected.

[2] "Qualitative Analysis," 7th Ed. p. 117 (1917).

[3] Noyes, *Loc. cit.*

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NOTES.

Changes in Volume during Solution. III.—A request for information as to the change in volume occurring during the solution in water of a certain substance for which experimental evidence is lacking, led to the devising of the following method, which, while it offers no new idea, still may be of interest:

The principle involved[1] is that the "apparent" volume of a salt in solution, *i. e.*, the difference between the volume of the water and volume of the solution, at high dilution is made up of two quantities determined by the nature of the ions of the salt. Although it is not possible to determine with certainty either of the two separately, the two together may be variously found, for instance by subtracting the change in volume when the salt dissolves from the volume of the salt. If the "apparent" volume concerned refers to equivalent amounts of material and is known for two pairs of ions, *i. e.*, potassium chloride and sodium bromide, as well as for one of the other two possible combinations, *i. e.*, sodium chloride, the "apparent" volume for the fourth combination, *i. e.*, potassium bromide, may be found by difference. Knowing the "apparent" volume in solution of potassium bromide as well as the molecular volume of potassium bromide, by subtraction one may find the change in volume during solution of potassium bromide.

In the following specimen calculations the data are taken from the paper of Baxter and Wallace[2] on changes in volume during the solution of the salts of the alkalies in water. The quantities are given in cc. and refer to gram molecular quantities of material at 25°.

POTASSIUM BROMIDE.

	KCl.	NaBr.	NaCl.
Molecular volume	37.5	33.1	27.0
Change in volume during solution at infinite dilution	—10.4	—7.9	—9.6
"Apparent" volume of salt in solution	27.1	25.2	17.4

"Apparent" volume of potassium bromide in solution = 27.1 + 25.2 — 17.4 = 34.9.

Change in volume during solution of potassium bromide at infinite dilution = 34.9 — molecular volume = 34.9 — 43.3 = — 8.4.

The observed value is — 8.8.

Lithium Iodide.

	LiCl.	CsI.	CsCl.
Molecular volume	20.5	57.6	42.4
Change in volume during solution of infinite dilution	—2.9	0.5	—2.4
"Apparent" volume of salt in solution	17.6	58.1	40.0

"Apparent" volume of lithium iodide in solution = 17.6 + 58.1 — 40.0 = 35.7.

Change in volume during solution of lithium iodide at infinite dilution = 35.7 — molecular volume = 35.7 — 33.0 = 2.7.

The observed value is 3.0.

The agreement of the calculated and observed values is satisfactory,

[1] Valson, *Compt. rend.*, 73, 441 (1871); and others.

[2] THIS JOURNAL, 38, 70 (1916).

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in view of the fact that the values at infinite dilution are all obtained by extrapolation. Furthermore it is worth while to call attention to the negative value obtained in the case of potassium bromide while lithium iodide yields a positive value.

At higher concentrations the method gives somewhat less satisfactory, although fairly accurate results. Since the "apparent" volume of a dissolved salt varies with the concentration, usually increasing with increasing concentration, it is necessary to use the appropriate values for the change in volume during solution.

The particular case at point is that of calcium carbonate, the solubility of which is so low as to preclude obtaining experimental evidence.

CALCIUM CARBONATE AT 25°.

	$CaCl_2$	Na_2CO_3	2NaCl
Molecular volume	51.6[1]	41.9[2]	54.0
Change in volume during solution at infinite dilution	—32.2[3]	—23.5[4]	—19.2
"Apparent" volume of salt in solution	19.4	18.4	34.8

"Apparent" volume of calcium carbonate in solution = 19.4 + 18.4 — 34.8 = 3.0.

Change in volume during solution of calcium carbonate at infinite dilution = 3.0 — molecular volume = 3.0 — 36.9[5] = —33.9.

This value for the contraction during solution is over 90% of the volume of the solid salt. Apparently the large contraction is about equally due to the calcium and the carbonate ions. GREGORY PAUL BAXTER.

T. JEFFERSON COOLIDGE, JR., CHEMICAL LABORATORY OF HARVARD COLLEGE, CAMBRIDGE, MASS.

Lecture Experiment on Vapor Pressure of Solutions.—The well-known fact that the vapor pressure of a liquid is lowered by a dissolved solid —provided the solid itself has no perceptible vapor pressure and the vapor consists of the pure solvent—is usually demonstrated *at room temperature*, by introducing the solutions and the solvent in the Torricellian vacuum of different barometer tubes. By mounting the tubes within a jacket, connected with a distilling flask, the phenomenon can be shown for any desired temperature, by choosing a suitable distilling liquid for keeping the tubes at the required temperature.

A very simple apparatus, by which it is possible to demonstrate the lowering of the vapor pressure at the *boiling point* (under atmospheric pressure) of the solvent—thus directly connecting with the ebullioscopic methods for molecular-weight determinations—is the following: A cylin-

[1] Richards and Hönigschmid, THIS JOURNAL, 33, 32 (1911).

[2] Richards and Hoover, *Ibid.*, 37, 105 (1915).

[3] Unpublished result by Baxter and Goode.

[4] Lamb and Lee, THIS JOURNAL, 35, 1685 (1913). (A small correction has been applied, since the experiments were made at 20°.)

[5] Landolt-Börnstein-Roth.

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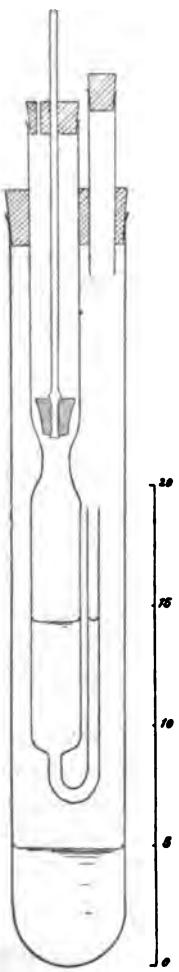
drical vessel, 30 cm. long with an inner bore of 5 cm.,[1] in which the solvent is boiled, serves as a constant temperature bath. This jacket is closed by a two-hole cork stopper, carrying a tube (inner bore 2 cm.) with a constriction half-way down and ending in a narrow tube (inner bore 5 mm)., bent upward as indicated in the figure. A short piece of glass tubing (inner bore 1 cm.) serving as outlet for the escaping vapor is run through the other hole in the stopper.

The inner tube can be shut off in the constricted part by a cork stopper, tightly held by a glass rod, which is loosely run through another cork, so as to allow an easy upward and downward movement of the rod. A ground-glass stopper affords a certain advantage, but is not absolutely necessary, provided gas-tight corks can be obtained. Pure solvent is poured in the outer jacket and also in the inner tube, filling both the wide and the narrow limb of the U-tube to a height of about 7 cm. above the bend. A trace of some anilin dye can be safely added in order to make any difference in level better visible at a distance. Owing to capillarity the liquid stands a little higher in the narrow (gage) tube. The difference in level may be neglected in a qualitative experiment of this kind, since it usually does not amount to more than two or three mm. The solvent in the jacket is then slowly heated over a small Bunsen or Teclu burner, suitably provided with a chimney, while the stopper is removed from the outlet tube. As soon as the vapor condenses on the walls of the outlet tube and escapes in the open, the air is removed and the outlet is closed. The vapor of the solvent then enters into the gage tube, heats the liquid in the test tube up to its boiling point, and escapes through the constricted neck, expelling at the same time the remaining air. After the vapor has bubbled through for a few minutes, the cork stopper—about 3 mm. above the neck—has been sufficiently heated and is pushed down, while at the same time the stopper is removed from the outlet tube, thus allowing the vapor to escape directly, as before in the open. The liquid in the inner tube ceases to boil, but is kept at constant temperature (the boiling point of the solvent) and is in equilibrium with its vapor. It will be seen that the level in the gage tube is practically the same as inside the test tube. The neck stopper is then removed and a weighed quantity, perhaps 0.3 g.,



[1] The exact dimensions may be derived from the figure, which includes a scale in cm. divisions.

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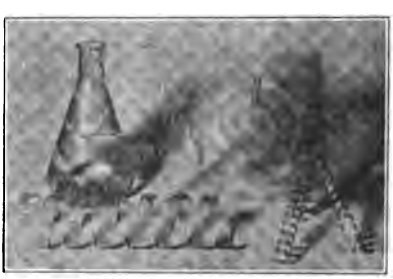
of some solid, easily dissolved in the chosen solvent, is introduced, preferably in the form of a tablet, and the operation is repeated. After equilibrium has been established, a difference in level of two or more cm. will be observed, the liquid standing at a lower level in the gage tube. On adding the same quantity of solute once more and repeating the above operation, the fall of the level in the narrow tube will be, on reaching equilibrium, about twice as much as before. A good solvent for a lecture demonstration is carbon tetrachloride, on account of its low boiling point (76°) its low surface tension (the capillary ascension being negligible) and its non-inflammability. As solute naphthalene or any other organic compound which can be compressed in tablets and dissolves readily in this solvent may be used.

The above-described method of heating the solution by means of the vapor of the solvent has been used by a great many investigators on ebullioscopic molecular-weight determinations: Sakurai, Landsberger, Walker and Lumsden, Ladenburg, Eykman, Smits, Beckmann, McCoy, and lately Menzies.[1] The last-named devised an apparatus similar to the one described here though more complicated, allowing quantitative measurements of molecular weights, solely based on the observed pressure differences, without any thermometer. The apparatus, proposed in this note, does not require for its construction any particular skill in glassblowing, can be easily set up and gives, in the limited time usually available for lecture experiments, very satisfactory results.

H. S. VAN KLOOSTER.

LAFAYETTE COLLEGE,
EASTON, PA.

A New Glass-Cutting Tool.—The cutting of large glass tubing with the hot point of a file is a common-place operation in chemical laboratories, but in the case of more complicated forms of apparatus the process is somewhat difficult and uncertain. Description is here given of a tool, constructed in this laboratory, which extends the method to a considerable degree. The fundamental requirement is a point that may be kept hot continuously; a crack once started should be kept moving in the right direction until the cut is completed; the success of the whole method depends upon the sudden, uniform expansion of a small area immediately in front of the crack.



The tool consists of a small, hollow head of brass or copper in which

[1] THIS JOURNAL, 32, 1615 (1910).

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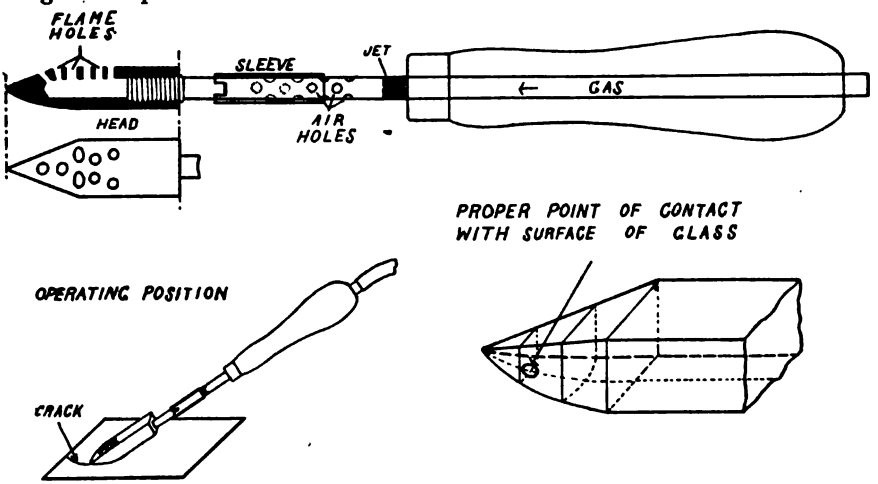
ordinary gas is burned, which is brazed or screwed onto a metal tube, through which the gas is supplied. The flow of gas should be regulated so that the flame will "strike back" and burn within the head. The diagram explains itself. The crack is started with a diamond or file



scratch and led in the desired direction with the hot, pointed end of the tool. The shape indicated has given the best results. With the head of the tool constantly red hot, it is an easy matter to cut glass into almost any shape desired, as indicated in the photograph.

KENNETH H. PARKER.

CHEMICAL LABORATORIES,
WILLIAM JEWELL COLLEGE,
LIBERTY, MISSOURI.

Substituting the Term Adduction for Oxidation.—The August number of THIS JOURNAL, page 1619, contains a short article on "Elements neither Free nor Combined. A Third State," in which I referred incidentally to substituting the term adduction for oxidation, giving what appeared to me to be good reasons. This being merely incidental in this article, I did not repeat the history of the term, as that was given by me in the second reference cited at the end as also on page 105 of a recently published book on "Electrochemical Equivalents." It was there acknowledged that this term was apparently first suggested for similar reasons by Dr. M. L. Hamlin in a paper by Nelson and Falk in THIS JOURNAL, 35, 1812 (1913), and independently by Dr. Frederick H. Getman in 1916, who had not seen this prior suggestion. I take pleasure in again repeating that the term was first suggested by Dr. Hamlin, and as there are very good reasons for its substitution for the antiquated, inconsistent and irrational term oxidation, I hope this new and rational term will meet with favor.

CARL HERING,

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A Method for Preventing Salts from Creeping over the Sides of Evaporating Dishes.—In the course of mineral or soil analysis it is frequently necessary to evaporate saline solutions to smaller volumes or to complete dryness to expel ammonium salts. When, during evaporation, the solution becomes saturated and solids separate on the sides of the dish, the deposited solids, particularly if calcium and magnesium chlorides be present along with ammonium chloride, have a tendency to draw the less concentrated solution further up the sides of the dish and deposit crystals there. If determinations are left to run overnight or unwatched in the daytime, they are frequently ruined in this manner.

Creeping can easily be prevented by painting a strip about $^1/_4$ inch wide around the inner rim of the dish with collodion. Salts will not creep over this strip. The collodion dries immediately after being put on so there is no time lost in this operation. The film contains no non-volatile residue and can easily be burned off.

W. O. ROBINSON.

BUREAU OF SOILS,
U. S. DEPARTMENT OF AGRICULTURE,
WASHINGTON, D. C.

CORRECTIONS.

On p. 1568 of our paper on Heterogeneous Equilibria between Aqueous and Metallic Solutions,[1] the statement is made that by the extrapolation of the logarithmic curve (curve No. 3, Fig. 4, p. 1563), a C_o value of 2.32 is obtained at an amalgam concentration of 0.225 milli-equivalent per 10 g. of mercury. And this value, 2.32, is subsequently made use of in the paper as the actual C_o value.

Also, on p. 1569, it is stated that C_o values at certain other amalgam concentrations are similarly obtained by the extrapolation of curves 1, 2 and 4, in Fig. 6.[2]

Owing to an unfortunate confusion of the zero point on the (log. total salt concn. × 10) abscissa, Fig. 4, p. 1563, with an actual salt concentration of zero, it was concluded that values of C_o could be obtained by the extrapolation of the logarithmic curves. This error has just been discovered. The values arrived at are not the C_o values in question, but the corresponding C_c values for the 0.1 N mixed salt solution (since 0 = log 0.1 × 10).

This error will necessitate a new study of the experimental data in the case of the sodium-strontium chloride mixtures; and this we hope to have ready for publication in the near future.

G. McP. SMITH AND S. A. BRALEY.

Nov. 17, 1917.

[1] THIS JOURNAL, 39, 1545 (1917).

[2] The statement should be "in Fig. 4;" owing to a typographical error, Fig. 6 is mentioned at this point.

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The formula given on p. 2297 in the November number of THIS JOURNAL in the paper entitled "Solubility and Internal Pressure" should have been written

$$\log N = \frac{-L(T_m - T)}{4.58TT_m}.$$

The correct form was used in the calculation of the data used in the paper.

The value N for anthracene in Table I on p. 2298 should be 0.0107.

JOEL H. HILDEBRAND.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF PITTSBURGH.]

PHTHALIC ACID DERIVATIVES; CONSTITUTION AND COLOR, V.[1] SOME DERIVATIVES OF TETRACHLORO- AND TETRAIODO PHTHALIMIDES.

BY DAVID S. PRATT AND GRANVILLE A. PERKINS.

Received October 17, 1917.

One of the most interesting sections in the vast field of investigation attempting more or less successfully to correlate constitution and color is the study of substances related to phthalic acid. Since the primary interest of such study, in the beginning if not now, was connected with visible color, investigations have dealt chiefly with the more complex members of the group, such as the phthaleins and related compounds. Such work was sufficient to establish certain theories of chromophores, auxochromes, etc., which must, however, be considered mere approximations. The *exact* correlation of absorption and constitution even in the simplest known substances seems at present such a complex affair that in the opinion of the authors it is not logical to expect to improve much on the present theories of color by a study confined to complicated substances such as the phthaleins or indeed any colored compounds. Our present knowledge indicates that while the physicist is approaching the problem of chemical affinity and its relation to radiant energy from the standpoint of molecular dynamics, the corresponding task of the organic chemist is to trace the relations between the absorption spectra of large numbers of closely related substances, thus linking the complex with the simple.

The already large literature dealing with absorption spectra unfortunately has the fault of being so detached in all but a few marked exceptions that it is generally impossible to trace accurately the connections between spectra even of substances in the same class. Information is lacking as a rule concerning the progressive changes brought

[1] For previous papers on simpler derivatives such as the anhydride, imide, oxime and anil see *Am. Chem. J.*, **47**, 89 (1912); *Phil. J. Sci.*, (*A*) **8**, 165, 399 (1913); *Ibid.*, **9**, 105 (1914).

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about by various steps leading from simple to complex derivatives. Thus, while it was a great step in advance several decades ago to connect the deep color of phenolphthalein salts with a quinoid arrangement of the molecule, neither this idea alone nor its amplifications have gone very far since then in correlating the absorption bands shown by various compounds related to the phthaleins, or towards ascribing to each a definite origin in the structure of the molecule. On the one hand, the quinoid rearrangement in itself seems insufficient to cause a deep purple color; on the other hand, deeply colored compounds are known, such as the salts of phthaloxime, where no quinoid arrangement seems possible.

It is the purpose, then, of this series of investigations to study the absorption spectra of a large number of compounds related to phthalic acid, each differing from its neighbors by minute steps only. It is hoped that the result will be a clearer insight into the relations between the absorption bands shown by different members of the same family and a more exact knowledge of the origin of each band.

The possible substitutions in the phthalic anhydride molecule fall naturally into three classes according to the position taken by the entering group. One or more hydrogens in the ring may be replaced, as in tetrachlorophthalic anhydride; oxygen in a carbonyl group may be substituted by a divalent radical or two monovalent atoms or radicals, and finally the anhydride oxygen may be replaced.

The present paper deals with the preparation of examples of the first and third types. Interesting molecular compounds were also encountered which do not come under the above classification since they are not substitution products. The absorption spectra of the various derivatives will be reported on at a later date since war conditions have made it impossible for the firm of Adam Hilger, London, to supply certain essential pieces of new apparatus ordered two years ago.

The replacement of hydrogen by halogen in the ring of phthalic acid was taken as the simplest example of this type of substitution. Here the effect of the change is known to be in general an increase in the period of vibration of whatever causes the main absorption bands, and a consequent shift toward the longer wave lengths. This fact is utilized commercially, tetrachloro- and 3,6-dichlorophthalic acids being well-known dye intermediates although the isomeric 3,4- and 4,5-dichloro acids have not been used so extensively. Studies of the imide derivatives of these partially chlorinated and a number of partially iodinated phthalic acids will appear in succeeding articles. Meanwhile the bromine series is being extensively studied.

Aside from being a series of preparations preliminary to spectroscopic study the investigation here reported brought to light an interesting type of molecular addition product; a new type of diphenyl amine derivative

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resulting from the introduction of an anilino group into the phthalic acid nucleus; and an interesting connection between dimorphism and "solvent of crystallization."

Preparation of the Imide Derivatives.

In passing spectroscopically from the halogen substituted anhydride to some other types such as the anil, oxime and phenylhydrazone, the imide was taken to serve as a connecting link. We have found it very convenient to convert various phthalic anhydrides into corresponding imides by gently warming them with formamide. The yields are excellent and contaminating products are not formed to any appreciable extent. Prolonged heating of tetrachlorophthalimide with formamide, however, carries the reaction further. While we have not succeeded in isolating any pure product from this second reaction, our analyses indicate a replacement of chlorine by an amino group.

The anils or phenylimides for the most part represented by $C_6X_4\langle{}^{CO}_{CO}\rangle N - C_6H_4R$ were readily prepared from the anhydride and amine. Generally acetic acid or nitrobenzene was used as a solvent. Difficulties experienced by previous investigators in preparing pure samples of halogenated phthalanils were mostly due to the effect of the amine upon the halogen. This reaction will be discussed after a consideration of the manner in which the amine breaks the anhydride ring.

The Action of Amines on the Anhydride Ring.

A fact which seems to have escaped notice hitherto is that certain amines give deeply colored unstable products with many substituted phthalic anhydrides. In some cases it is possible to isolate the addition products, in others the reaction, if it may be so called, is evidenced only by the color produced. Tetrachlorophthalic anhydride, for example, gives with dimethylaniline a 1 : 1 molecular addition product which crystallizes in intensely red prisms. That this reaction does not depend on the chlorine is shown by a similar crystalline product prepared[1] from 3-nitrophthalic anhydride, and colors produced with a number of other substituted phthalic anhydrides. The unsubstituted anhydride gives an orange color when dissolved in dimethyl aniline. In fact, sufficient examples of this reaction have been tried besides those directly within the scope of this article to warrant the conclusion that aromatic amines, perhaps all amines, form as a *first* step in their reactions with phthalic anhydride and its nuclear substituted derivatives a molecular addition product.

The structural formula to be assigned such a compound is doubtful as in all such cases. Chemists are wont to pick out the main or primary

[1] By A. B. Coleman.

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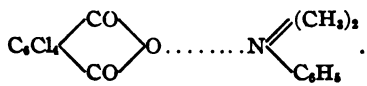
forces which hold atoms together, represent them by "bonds," and consider the secondary forces relatively unimportant. Taking into account, however, their undoubted relations to the absorption of light by the molecule, a knowledge of the secondary forces is essential from the point of view of the spectroscopic study in hand. What, then, can we say of the forces which unite a tetrachlorophthalic anhydride molecule to a dimethylaniline molecule with the production of a deep red color? The most reasonable point of attachment on the amine molecule would seem to be the nitrogen, known to have "residual valency." In the other molecule the anhydride ring is evidently responsible for the union, which may accordingly be expressed



Perhaps the uniting forces engage the carbonyl groups more directly than is here indicated; the dotted line merely shows approximately what we consider the points of attachment.

The production of a deep color by such an unstable union is a phenomenon often observed. Accepting for the sake of definiteness the view that visible absorption is caused primarily by the vibration of valence electrons,[1] it is probable that here the union or conjugation through secondary atomic forces has caused a remarkable weakening of one or more valence fields. In other words, it has greatly lowered the potential gradients surrounding one or more valence electrons, thus allowing them to vibrate in periods corresponding to the frequency of visible light instead of the ultraviolet rays which they formerly absorbed. Another possibility is that certain "residuary" valence electrons, not recognized in Stark's hypothesis, have had their surrounding fields strengthened so that their absorption is shifted into the visible from the infra red. A decision between these two possibilities can probably be arrived at by a spectroscopic study of sufficient related complexes to trace the main visible absorption from its origin in the ultraviolet or infra red. The first-mentioned alternative is certainly the most usual effect of conjugation.

Considering, then, that certain force fields are weakened the next step in the reaction seems quite natural. With tertiary amines, indeed, no further step is possible, but in case the amine is secondary a rearrangement quickly takes place, while with primary amines three steps may be observed. For example, aniline added to a benzene solution of tetrachlorophthalic anhydride gives first a transitory yellow color (I), immediately followed by a white precipitate of aniline tetrachlorophthalanilate (II), which when warmed gives off aniline and water forming the anil (III).

[1] J. Stark, "Die Electrizitat im chemischen Atom," Leipzig, 1915.

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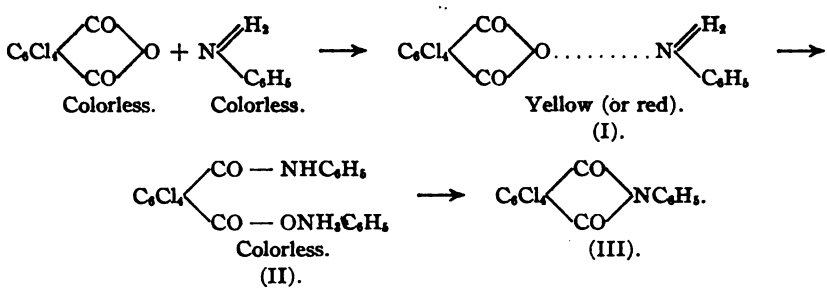
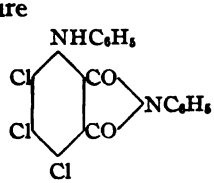


It seems probable that primary amines in general react with phthalic anhydrides in the three steps illustrated above giving imides, anils, oximes, or hydrazones according to the nature of the amine. Although most amines give little or no color as a result of the first step, a few produce a deep red (*e. g.*, α-naphthylamine and tetrachlorophthalic anhydride). The second step might perhaps better be represented as a simple rearrangement to the amic acid which would then react with another molecule of amine forming the salt shown in (II). The precipitate actually obtained, however, was the salt, not the amic acid. The third step, *i. e.*, the closing of the imide ring, has been studied from a theoretical standpoint by Tingle.[1] Our interest in this reaction was more from a practical point of view. Almost the only difficulty experienced in the preparation of halogenated phthalanils was due to the further effect of amines upon them.

The Action of Aniline upon Halogen in the Nucleus.

After an amine has reacted completely with the anhydride ring of the halogenated phthalic molecule it shows a tendency to attack the halogen. Long boiling with aniline converts tetrachlorophthalanil, for example, into a tarry mixture from which a monoanilino and a dianilino product were isolated. The structure



seems a probable one for the monoanilino anil but it is also possible that the anilino group takes the 4-position. An attempt to establish the structure of the dianilino product will be described in the seventh paper of this series. Attempting to prepare some dianilino-dichlorophthalanils from diiododichlorophthalanils of known structure, we have so far succeeded in obtaining only one, the 3,6-dianilino-4,5-dichloro derivative. This was found to be different from the product from tetrachlorophthalanil, but

[1] This Journal, 32, 1319 (1910).

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since we were unable to purify it too much reliance should not be placed on the difference.

The monoanilino product from tetrachlorophthalanil is orange, the dianilino derivative red. This new class of compounds has such possibilities from the standpoint of color that we have continued its investigation. The next paper of this series will be devoted to the anilino products from some dichlorophthalanils. These give better yields and a better opportunity for determination of structure.

Dimorphism in the Anils.

Tetrachlorophthal-*p*-tolil was found to exhibit dimorphism in that it was obtained both as colorless, hexagonal leaflets and as long, hair-like, yellow needles. Either form can be converted easily into the other without change in weight, and so readily that actual structural isomerism is improbable. The colorless form is stable at ordinary temperatures, does not combine with solvent of crystallization and melts at 207° (corr.). The yellow form is unstable except above 118°, combines with many solvents, and melts at 214–214.5° (corr.).

Dimorphic forms of anils have been reported by Chattaway[1] who recorded a few similar cases but without giving different melting points for the two forms or any tendency of one to add solvent of crystallization. The unstable form must possess more free energy below its transition point than the colorless modification. The corresponding greater unsaturation in its valency fields is evidenced by the tendency to form coördination products by conjugation with solvents such as benzene *m*-xylene, nitrobenzene and dimethylaniline. For the reason given above this difference in valency fields is not to be attributed to actual isomerism, but to the different intermolecular effect caused by differing crystal structure.

The addition products with solvents do not show a molecular ratio of one to one; our results with different solvents vary from 1 : 3 to 1 : 5. One molecule of dimethylaniline, for example, apparently combines with five molecules of the *p*-tolil. This is so different from its action with tetrachlorophthalic anhydride that the two cases are hardly comparable; both products, however, have a deep red color.

Dimorphism was found to be very common among phthalimide derivatives. The cases of 3,4-dichlorophthalanil, 3-anilino-6-chloro-phthalanil, and 4,5-diiodophthalanil will be considered in the two succeeding papers of this series.

Experimental.

Tetrachlorophthalic Acid.—The tetrachlorophthalic acid used for a part of this work was the commercial product purified by Delbridge's[2] method. We found it necessary, however, to use twice as much sodium hydroxide

[1] *J. Chem. Soc.*, **109**, 89 (1916).

[2] *Am. Chem. J.*, **41**, 414 (1909).

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as he recommends. The acid was conveniently changed to anhydride by recrystallization from acetic acid.

After the commercial supply had been cut off tetrachlorophthalic anhydride was prepared from phthalic anhydride.[1]

500 g. of phthalic anhydride, 2 kg. of 50% fuming sulfuric acid, and 10 g. of iodine were the proportions we used. The mixture was heated in an oil bath to 70° and a stream of chlorine passed through for about 40 hours. During the first few hours the temperature was increased to about 100°, and there maintained until the last few hours, when it was raised to 180°. The mixture was transferred to a porcelain dish, allowed to cool, and treated slowly with water. The tetrachlorophthalic anhydride, which separated in well-formed crystals, was freed from sulfuric acid by digestion with water at 100°. It melted at 255–256.5° (corr.) without further purification. Delbridge gives 255–257° (corr.) for the pure substance.

Addition Product with Dimethylaniline.—Tetrachlorophthalic anhydride is very soluble in warm dimethylaniline, giving an intensely red solution which deposits large red prisms on cooling. These crystals readily effloresce on exposure to air or on washing with organic solvents, giving off dimethylaniline and leaving the anhydride as a somewhat contaminated light yellow powder.

Exact analysis was prevented by the difficulty of freeing the crystals entirely from mother liquor without efflorescence taking place. A close approximation, however, was not found difficult. Sample No. I was prepared by drying fresh crystals on paper as well as possible without much crushing and then exposing to the air overnight. Six hours at 100° sufficed to drive off the solvent of crystallization. Sample No. II was prepared by leaving fresh crystals 10 days in a desiccator containing tetrachlorophthalic anhydride to absorb excess of solvent.

Subst. (I) 2.9718, (II) 0.2906.
Loss (6 hours at 100°): (I) 0.8900, (II) 0.0844.
Calc. for $C_8O_3Cl_4.C_6H_5N(CH_3)_2$: loss, 29.8%. Found: (I) 30.0, (II) 29.0.

Addition Product with Dimethyl-*p*-toluidine. — Tetrachlorophthalic anhydride combines with dimethyl-*p*-toluidine just as with dimethylaniline, but the product has a deeper, almost purple color. The crystals obtained were contaminated with a small amount of a colorless substance, probably the salt. Sample No. I was prepared by allowing the crystals to stand exposed until a very slight efflorescence was observed. This required 23 hours. The loss was determined as before. Sample No. II was prepared by drying fresh crystals 10 days in a desiccator containing excess anhydride.

[1] Juvalta, D. R. P. 50,177; *Fortschr. Teerfarb.-fabrik.*, **2**, 93 (1889).

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Subst. (I) 0.9520, (II) 0.2475.
Loss (6 hours at 100°): (I) 0.2897, (II) 0.0696.
Calc. for $C_8O_3Cl_4.C_7H_7N(CH_3)_2$: loss, 32.4%. Found: (I) 30.4, (II) 28.1.

Action of Other Tertiary Amines.—Tetrachlorophthalic anhydride gives a red color with diethylamine but crystallizes out unchanged. Pyridine gives no color. Triethylamine gives little or no color.

Action of Secondary Amines.—Monomethylaniline gives a deep red with tetrachlorophthalic anhydride. The anhydride slowly dissolves, the color fades, and disappears. In xylene solution the same fading color is produced. No precipitate is formed. Diphenylamine in xylene solution gives an orange color.

Action of Primary Amines.—α-Naphthylamine in xylene solution gives a deep red color and a white precipitate when added to a xylene solution of tetrachlorophthalic anhydride. The color persists for some hours in the cold, but disappears on long standing or warming. β-Naphthylamine in xylene solution gives an orange-red color, which quickly fades leaving a white, gelatinous precipitate. Aniline gives a transient yellow color, immediately forming white aniline tetrachlorophthalanilate.

Tetrachlorophthalimide.—Graebe[1] prepared this substance by the action of ammonia gas on the melted anhydride and stated that it melts "near the boiling point of mercury." We preferred the following method: Ten grams of powdered tetrachlorophthalic anhydride were dissolved by warming with 100 g. of formamide. Soon the imide began to precipitate, and after five minutes' gentle heating it was filtered off without cooling, and washed with alcohol. Ten grams of anhydride were added to the filtrate and the process repeated. The combined yield, about 90% of theoretical, was 18 g. of colorless blades, which melted at 338–339° (corr.) after recrystallization from acetic acid. Very slow heating gives a slightly lower melting point. This forms an exceptionally good method for making imides of halogenated phthalic anhydrides.

The imide was analyzed for chlorine by the lime combustion method.

Subst. (I) 0.2615, (II) 0.4308; cc. 0.1 *N* $AgNO_3$, (I) 36.82, (II) 60.46.
Calc. for $C_8HO_2NCl_4$: Cl, 49.79. Found: (I) 49.93, (II) 49.77.

One gram of the imide dissolves in 100 cc. of boiling acetic acid. It is more soluble in nitrobenzene and readily dissolved by pyridine. The alkali salts are colorless and insoluble in water.

Action of Formamide on Tetrachlorophthalimide.—The light yellow-colored formamide filtrate from the preparation of tetrachlorophthalimide was treated with 10 g. more of anhydride, then heated 45 minutes to dissolve the imide formed, and finally boiled briskly for 10 minutes. The solution, which was deep red with a strong green fluorescence, gave

[1] *Ann.*, **238**, 332 (1887).

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no deposit on standing overnight, showing that the imide had practically disappeared. About 5 g. of an impure green product were obtained by boiling with water, cooling and filtering. This melted at about 313° (corr.) after two recrystallizations from alcohol.

Subst. 0.0851; cc. 0.1 *N* $AgNO_3$, 11.16.
Calc. for $C_8HO_2NCl_4$: Cl, 49.79.
Calc. for $C_8H_2O_2N_2Cl_3$: Cl, 40.07. Found: 45.98.

The chlorine analysis indicates that some of the chlorine had been removed from the imide, but not sufficient to represent the replacement of one atom by an amino group. A Kjeldahl analysis was made.

Subst. 0.0812; cc. 0.1 *N* HCl, 3.61.
Calc. for $C_8HO_2NCl_4$: N, 4.92.
Calc. for $C_8H_2O_2N_2Cl_3$: N, 10.55. Found: 6.23.

This analysis indicates that the chlorine missing in the previous analysis has been replaced by the amino group. Further experiments were made, including the use of acetamide which seems to act like formamide except more slowly, but no pure product was obtained.

Aniline Tetrachlorophthalanilate.—Six grams of tetrachlorophthalic anhydride were dissolved in hot benzene and a solution of two grams of aniline in benzene slowly added. The first addition gave a yellow color quickly followed by a white precipitate, but precipitation was still incomplete after addition of all the aniline. Since slightly over one molecular equivalent had been added the precipitate must have contained more than one mol of amine per mol of anhydride. A further addition of 2 g. of aniline in benzene completed the precipitation. The product was filtered off and recrystallized from alcohol. The mixture was boiled with benzene to remove some anil formed in the reaction.

Analysis:[1]

Subst. (I) 0.2520, (II) 0.1879; cc. 0.1 *N* HCl, (I) 9.90, (II) 7.50.
Calc. for $C_{20}H_{14}O_3N_2Cl_4$: N, 5.94. Found: (I) 5.50, (II) 5.59.

Since the benzene had apparently removed a little aniline from the salt, it was boiled with benzene containing a small amount of aniline.

Subst. (I) 0.1490, (II) 0.1639; cc. 0.1 *N* HCl, (I) 6.26, (II) 6.91.
Calc. for $C_{20}H_{14}O_3N_2Cl_4$: N, 5.94. Found: (I) 5.89, (II) 5.91.

Subst. (I) 0.2322, (II) 0.2871; cc. 0.1 *N* $AgNO_3$, (I) 19.68, (II) 24.36.
Calc. for $C_{20}H_{14}O_3N_2Cl_4$: Cl, 30.05. Found: (I) 30.05, (II) 30.09.

Aniline tetrachlorophthalanilate dissolves in about ten parts of boiling alcohol from which it separates on cooling in a white crystalline powder mixed with leaflets of the anil. It is insoluble in benzene, but very

[1] Kjeldahl determinations of nitrogen required the modifications suggested in *Z. anal. Chem.*, **31**, 525 (1892); Conn. Agr. Exp. Sta., *Rep.* **190** (1898) and long-continued boiling, otherwise the results were invariably low. This method was used in all the nitrogen analyses reported in this paper.

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soluble in acetic acid, quickly forming the anil. The purified salt melted at 271–273° (corr.) on rapid heating.

Tetrachlorophthalanil.—This substance was prepared by Graebe's[1] method, by the method of Tingle and Bates,[2] and also by heating the anhydride in aniline. None of these methods, however, was as satisfactory as adding aniline to a boiling solution of the anhydride in acetic acid. The resulting product is nearly pure, and forms leaflets of rhombic outline. These are almost colorless, but have, especially when the crystals are large, a pale yellow cast not removed by several recrystallizations.

Subst. (I) 0.1566, (II) 0.1409; cc. 0.1 *N* $AgNO_3$, (I) 17.33, (II) 15.59.
Calc. for $C_{14}H_5O_2NCl_4$: Cl, 39.30. Found: (I) 39.24, (II) 39.24.

Subst. (I) 0.3113, (II) 0.2607; cc. 0.1 *N* HCl, (I) 8.34, (II) 7.21.
Calc. for $C_{14}H_5O_2NCl_4$: N, 3.88. Found: (I) 3.75, (II) 3.87.

Tetrachlorophthalanil was found to melt at 274–275° (corr.). (Graebe and Buenzod record 268–269°.) It is soluble in ethyl acetate, acetone, benzene and acetic acid, very slightly in ether or alcohol, insoluble in petroleum ether.

No addition products of the anil with solvents were isolated. It gives a deep red color with dimethylaniline or dimethyl-*p*-toluidine, and a lighter red with dimethyl-*o*-toluidine, but crystallizes from these solvents in the original colorless form.

3-Anilino-4,5,6-trichlorophthalanil (4,3,5,6,?). — One part of tetrachlorophthalic anhydride was boiled gently for three hours in four parts of aniline. It was found advisable to avoid oxidation of the aniline by using an inactive atmosphere such as natural gas. Acetic acid was added to the product and the mixture poured into dilute hydrochloric acid. The precipitate was filtered off and recrystallized, using boneblack, once from acetic acid and several times from alcohol. Orange blades were obtained melting at 179.5–180.5° (corr.).

Subst. (I) 0.2869, (II) 0.2612; cc. 0.1 *N* $AgNO_3$, (I) 20.56, (II) 18.82.
Calc. for $C_{20}H_{11}O_2N_2Cl_3$: Cl, 25.48. Found: (I) 25.41, (II) 25.55.

Subst. (I) 0.2294, (II) 0.2396; cc. 0.1 *N* HCl, (I) 11.02, (II) 11.50.
Calc. for $C_{20}H_{11}O_2N_2Cl_3$: N, 6.71. Found: (I) 6.73, (II) 6.72.

One gram of the anilino anil dissolves in 5 cc. of boiling acetic acid or in 100 cc. of boiling alcohol.

Dianilino-dichlorophthalanil.—A small quantity of this substance was isolated from the mother liquors of the monoanilino product. More was obtained by increasing the time of boiling with aniline to 24 hours. The product, after purification as described for the monoanilino anil, was a very small yield of bright scarlet blades melting at 182.5–183.5° (corr.). It is somewhat more soluble than the monoanilino derivative.

[1] *Ber.*, **32**, 1994 (1899).
[2] THIS JOURNAL, **32**, 1325 (1910).

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Subst. (I) 0.1463, (II) 0.0969, (III) 0.1571; cc. 0.1 *N* $AgNO_3$, (I) 6.31, (II) 4.18, (III) 6.72.

Calc. for $C_{26}H_{17}O_2N_3Cl_2$: Cl, 14.96. Found: (I) 15.28, (II) 15.30, (III) 15.17.

Subst. 0.1835; cc. 0.1 *N* HCl, 11.12.

Calc. for $C_{26}H_{17}O_2N_3Cl_2$: N, 8.87. Found: 8.49.

Tetrachlorophthal-*o*-tolil.—Ten grams of the anhydride were boiled with 50 cc. of acetic acid, 20 g. of freshly distilled *o*-toluidine added, and the boiling continued a few seconds. The product was filtered off after cooling and recrystallized twice from acetic acid using boneblack. About 8 g. of colorless rhombic leaflets were thus obtained, having a melting point of 232–236.5° (corr.) unchanged by recrystallization.

Subst. (I) 0.2093, (II) 0.2164; cc. 0.1 *N* $AgNO_3$, (I) 22.46, (II) 23.26.

Calc. for $C_{15}H_7O_2NCl_4$: Cl, 37.83. Found: (I) 38.05, (II) 38.11.

The *o*-tolil has about the same solubilities as the anil. One gram dissolves in 40 cc. of boiling acetic acid.

Tetrachlorophthal-*m*-tolil.—Ten grams of powdered anhydride were boiled with 30 cc. of acetic acid and 20 g. of freshly distilled *m*-toluidine added. The procedure was continued as with the *o*-tolil, resulting in 8 g. of colorless rhombic leaflets of constant melting point 245.5–246.5° (corr.). One gram dissolves in 80 cc. of boiling acetic acid.

Subst. (I) 0.3122, (II) 0.2727; cc. 0.1 *N* $AgNO_3$, (I) 33.41, (II) 29.23.

Calc. for $C_{15}H_7O_2NCl_4$: Cl, 37.83. Found: (I) 37.95, (II) 38.01.

Tetrachlorophthal-*p*-tolil.—Twenty grams of tetrachlorophthalic anhydride were dissolved in 250 cc. of boiling acetic acid, 20 g. of recrystallized *p*-toluidine acetate added, and the boiling continued a few minutes. The product was filtered off after cooling and recrystallized from acetic acid.

Subst. (I) 0.1815, (II) 0.1483; cc. 0.1 *N* $AgNO_3$, (I) 19.39, (II) 15.82.

Calc. for $C_{15}H_7O_2NCl_4$: Cl, 37.83. Found: (I) 37.88, (II) 37.83.

Subst. (I) 0.2876, (II) 0.3176; cc. 0.1 *N* HCl, (I) 7.73, (II) 8.47.

Calc. for $C_{15}H_7O_2NCl_4$: N, 3.74. Found: (I) 3.77, (II) 3.74.

Dimorphism.

Tetrachlorophthal-*p*-tolil usually crystallizes from acetic acid or alcohol in colorless hexagonal leaflets. This modification is stable at ordinary temperatures and even at the boiling point of acetic acid, but when heated to 207° (corr.), it softens and turns yellow, giving a second modification, which is stable at that temperature, and melts at 214–214.5° (corr.). The melting point of the colorless modification was determined by dipping successive samples contained in capillary tubes into the melting point bath at various known temperatures. At 206° (corr.) no change could be observed. At 207° the sample melted to a cloudy liquid, immediately turning yellow. At 210° a fresh sample melted to a clear liquid, which did not immediately solidify, but when removed from the bath im-

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mediately changed to a yellow solid that did not melt on returning to the bath at 210°.

It is evident that tetrachlorophthal-*p*-tolil has a transition point between 118° and 207°. The rate of transformation is so slow even at high temperatures, that the colorless form may be heated slowly to its melting point without changing to the yellow form. Just as it begins to melt, at 207° (corr.), transformation rapidly sets in, and the fact that the yellow form is much more stable at this temperature is shown by the difference of 7° between the melting points.

The yellow form of tetrachlorophthal-*p*-tolil may sometimes be obtained by dissolving the leaflets in acetic acid or alcohol and allowing the warm solution to stand undisturbed. Seeding with the yellow form insures the result. Long hair-like needles appear which spread through the solution so much faster than the more stable leaflets that almost the entire quantity may be obtained in the unstable modification. This may be kept a few days in the dry condition, but in contact with solvent soon changes to colorless leaflets. The transformation takes place without change in weight, showing that no solvent of crystallization is involved.

Addition Products with Solvents.

Tetrachlorophthal-*p*-tolil forms colored addition products with solvents such as benzene, xylene, nitrobenzene, dimethylaniline, etc. The colorless modification, however, does not appear to react with the vapors of these substances. A sample of this form was powdered and exposed to air nearly saturated with benzene vapor for several days. The powder did not increase in weight or change color even after a small spot was moistened with benzene. The spot remained yellow, but did not spread, which shows the inability of the colorless modification to take up benzene. In contact with liquid benzene, however, it immediately forms the yellow addition product. In fact, none of the above-named solvents have been observed to deposit the *p*-tolil except as an addition product (cf. acetic acid and alcohol).

The action of dimethylaniline vapor is prettily shown by melting some *p*-tolil on a watch-glass and cooling in such a manner that part remains yellow and part becomes white, seeding with the colorless form if necessary. On exposure to the vapor of dimethylaniline in a desiccator, the yellow part quickly becomes a deep red while the white remains unaffected.

Addition Product with Benzene.—The *p*-tolil separates from benzene solution in long hair-like yellow crystals. If not broken up these are fairly stable in air. In the first determination the sample taken was some of the pure *p*-tolil which was then left in a desiccator with benzene. Here the air was saturated with benzene vapor, so that the sample became moist and formed the addition product. After several hours the

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excess benzene was allowed to evaporate in the open air, requiring about 8 hours for practically constant weight. The percentage was calculated not on the weight of sample but on the weight of addition product, to correspond with the following determinations: Sample No. 2 was composed of well-formed crystals from benzene, air-dried to constant weight (12 hours). The sample rapidly lost weight on being ground by a small pestle, included in the tare, and came to constant weight in 3 hours at 100°. Sample No. 3 had been kept six months, and showed decomposition only by a slight dullness of the crystals. The benzene was removed by adding alcohol and heating to 100°, repeating to constant weight. Sample No. 4 was prepared by allowing fresh crystals to stand in a desiccator containing some yellow *p*-tolil to absorb the excess benzene. The benzene of crystallization was removed from this and the following samples by adding ethyl acetate and heating to 100°. This was found to be the quickest method. Sample No. 5 was dried 30 minutes in air and 15 minutes *in vacuo*. Samples No. 6 and No. 7 were dried 5 minutes in air and 10 minutes *in vacuo*.

Subst. (I) 0.7173, (II) 0.4926, (III) 0.5964, (IV) 0.5466, (V) 1.0337, (VI) 0.8319, (VII) 1.0591. Loss: (I) 0.0423, (gain): (II) 0.0315, (III) 0.0326, (IV) 0.0310, (V) 0.0561, (VI) 0.0472, (VII) 0.0602.

Calc. for $(C_{15}H_7O_2NCl_4)_3.C_6H_6$: loss, 6.49%. For $(C_{15}H_7O_2NCl_4)_4.C_6H_6$: loss, 4.95%. Found: (I) 5.57, (II) 6.39, (III) 5.47, (IV) 5.67, (V) 5.43, (VI) 5.67, (VII) 5.68.

Apparently the ratio of *p*-tolil molecules to benzene molecules was between 3 and 4.

Addition Product with *m*-Xylene.—Sample No. I was crystallized from *m*-xylene and exposed to the air 12 hours. Sample No. II was dried in air 1 hour after which it lost practically no weight during 15 minutes *in vacuo*. Both samples were decomposed by ethyl acetate and heated to 100°.

Subst. (I) 0.4167, (II) 1.0001; loss, (I) 0.0263, (II) 0.0633.
Calc. for $(C_{15}H_7O_2NCl_4)_4.C_8H_{10}$: loss, 6.61. Found: (I) 6.31, (II) 6.33.

Addition Product with Nitrobenzene.—Sample No. I was crystallized from nitrobenzene, washed rapidly with petroleum ether, and exposed 30 minutes to the air, after which it lost no more weight *in vacuo* during 15 minutes. The solvent of crystallization was driven off by adding acetic acid and heating to 110°. A repetition of this treatment caused no further loss in weight. Sample No. II was treated in practically the same manner.

Subst. (I) 0.7423, (II) 1.0922; loss, (I) 0.0539, (II) 0.0851.
Calc. for $(C_{15}H_7O_2NCl_4)_4.C_6H_5O_2N$: loss, 7.58. Found: (I) 7.26, (II) 7.79.

The product is yellow like that from benzene, but has more the appearance of blades.

Addition Product with Dimethylaniline.—Tetrachlorophthal-*p*-tolil is quite soluble in dimethylaniline and crystallizes out in scarlet needles.

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The fresh crystals were washed with petroleum ether. Almost no loss in weight was observed when the first sample was dried in air one hour, and the second *in vacuo* ten minutes. Ethyl acetate was employed as before to remove the solvent of crystallization.

Subst. (I) 0.7486, (II) 1.3563; loss, (I) 0.0498, (II) 0.0880.
Calc. for $(C_{15}H_7O_2NCl_4)_4.C_8H_9N$: loss, 7.47.
Calc. for $(C_{15}H_7O_2NCl_4)_5.C_8H_9N$: loss, 6.07. Found: (I) 6.65, (II) 6.49.

The observed loss represents a molecular ratio of nearly 5 to 1.

Tetrachlorophthal-*o*-nitroanil.—Twenty grams of the anhydride and 10 g. of *o*-nitraniline were boiled one-half hour in 200 cc. of acetic acid. The crystals were filtered off on cooling and the filtrate evaporated to one-third to recover more of the product. The total yield, about 70% of the theoretical, was 20 g. of colorless leaflets. These, after crystallization from benzene using boneblack, showed a melting point of 272–273° (corr.) unchanged by recrystallization from xylene.

Subst. (I) 0.2475, (II) 0.1432; cc. 0.1 *N* $AgNO_3$, (I) 24.66, (II) 14.26.
Calc. for $C_{14}H_4O_4N_2Cl_4$: Cl, 34.94. Found: (I) 35.33, (II) 35.31.

One gram of the *o*-nitroanil dissolves in 40 cc. of boiling benzene or 12 cc. of boiling xylene. It is quite soluble in acetic acid, slightly in ethyl acetate, almost insoluble in alcohol.

Tetrachlorophthal-*m*-nitroanil.—Twenty grams of the anhydride in 600 cc. of acetic acid were boiled one-half hour with 10 g. of *m*-nitraniline. The product after cooling was filtered off and recrystallized from acetic acid and xylene, giving almost colorless blades of melting point 300–301.5° (corr.) unchanged by recrystallization from xylene. The final product weighed 14 g.

Subst. (I) 0.2459, (II) 0.1752; cc. 0.1 *N* $AgNO_3$, (I) 24.37, (II) 17.44.
Calc. for $C_{14}H_4O_4N_2Cl_4$: Cl, 34.94. Found: (I) 35.14, (II) 35.30.

One gram of the *m*-nitroanil dissolves in 150 cc. of boiling acetic acid or 50 cc. boiling xylene.

Tetrachlorophthal-*p*-nitroanil.—Fifteen grams of *p*-nitraniline were added to a boiling solution of 30 g. of tetrachlorophthalic anhydride in 400 cc. of acetic acid. The mixture was boiled 15 minutes and then heated an hour in a water bath. The fine, colorless needles obtained were recrystallized from benzene using boneblack. The product then had a melting point of 292–297° (corr.), unchanged by repeating the treatment. One gram of the substance dissolves in 100 cc. of boiling benzene.

Subst. (I) 0.1545, (II) 0.2035; cc. 0.1 *N* $AgNO_3$, (I) 15.27, (II) 20.09.
Calc. for $C_{14}H_4O_4N_2Cl_4$: Cl, 34.94. Found: (I) 35.05, (II) 35.01.

Tetrachlorophthal-*p*-hydroxyanil. — Twenty grams of tetrachlorophthalic acid were dissolved in 100 cc. of acetic acid and boiled to form the anhydride. Ten grams of *p*-aminophenol were then added and the boiling continued 5 minutes. Twenty-two grams, an 89% yield, of

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bright yellow needles were filtered off after cooling. On recrystallization from acetic acid the melting point was 305–307° (corr.) unchanged by recrystallization from xylene.

Subst. (I) 0.2142, (II) 0.2970; cc. 0.1 *N* $AgNO_3$, (I) 22.73, (II) 31.37.
Calc. for $C_{14}H_8O_2NCl_4$: Cl, 37.63. Found: (I) 37.63, (II) 37.45.

One gram of the *p*-hydroxyanil dissolves in 100 cc. of boiling acetic acid or about 120 cc. of boiling xylene.

Tetrachlorophthal-*p*-acetylaminoanil.—*p*-Amino acetanilide was prepared by reducing the nitro compound following Nietzki's directions.[1]

Twenty grams of tetrachlorophthalic acid were boiled in 800 cc. of acetic acid, forming the anhydride. A solution of 10 g. of *p*-amino acetanilide in 200 cc. of acetic acid was added and the boiling continued 10 minutes. Twenty-five grams of product, an 86% yield, were filtered off after cooling. This was recrystallized twice from acetic acid, using boneblack.

Subst. (I) 0.2165, (II) 0.2181; cc. 0.1 *N* $AgNO_3$, (I) 20.79, (II) 20.84.
Calc. for $C_{16}H_8O_3N_2Cl_4$: Cl, 33.93. Found: (I) 34.05, (II) 33.88.

The *p*-acetylaminoanil melts with decomposition at about 339° (corr.). One gram dissolves in 100 cc. of boiling acetic acid, from which it crystallizes in a mixture of pale yellow warts and very small, colorless needles. It is readily dissolved by pyridine.

Tetraiodophthalimide.—Fifty grams of tetraiodophthalic anhydride[2] in 150 cc. of nitrobenzene were treated with 50 g. of formamide and boiled one-half hour. The yield was 30 g., about 60%, a part of which was recrystallized twice from nitrobenzene.

Subst. (I) 0.5222, (II) 0.3366; cc. 0.1 *N* $AgNO_3$, (I) 32.40, (II) 20.97.
Calc. for $C_8HO_2NI_4$: I, 78.02. Found: (I) 78.57, (II) 79.07.

One gram of the imide dissolves in 70 cc. of boiling nitrobenzene, from which it crystallizes in fine, yellow needles melting at about 370–380° (corr.) with decomposition. It is moderately soluble in aniline, phenol and pyridine but not in the ordinary solvents.

Tetraiodophthalanil.—Twenty grams of the anhydride were dissolved in 100 cc. of boiling nitrobenzene and 10 cc. of aniline added. A yield of 18 g., 82%, was obtained. This was recrystallized twice from xylene and twice from nitrobenzene. Its melting point of 314–315° (corr.) was unchanged by the last crystallization.

Subst. (I) 0.3619, (II) 0.2469; cc. 0.1 *N* $AgNO_3$, (I) 20.08, (II) 13.80.
Calc. for $C_{14}H_8O_2NI_4$: I, 69.85. Found: (I) 70.42, (II) 70.94.

One gram of the anil dissolves in 8 cc. of boiling nitrobenzene from which it separates in yellow blades. It is about one-half as soluble in xylene, and nearly insoluble in acetic acid.

[1] *Ber.*, **17**, 343 (1884); **33**, 191 (1900).

[2] Detailed directions for preparing the tetraiodophthalic anhydride will appear in a later article by Pratt and Shupp on phenoltetraiodophthalein.

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Tetraiodophthal-*o*-tolil.—Thirty grams of the anhydride were dissolved in 80 cc. of boiling nitrobenzene and 7 g. of *o*-toluidine added. The mixture was boiled a minute and allowed to cool. A yield of 27 g., 79%, was obtained. This was recrystallized from xylene using boneblack, having then a melting point of 314–315° (corr.) unchanged by recrystallization.

Subst. (I) 0.3687, (II) 0.3303; cc. 0.1 *N* $AgNO_3$, (I) 20.21, (II) 18.10.
Calc. for $C_{15}H_7O_2NI_4$: I, 68.53. Found: (I) 69.57, (II) 69.55.

One gram of the *o*-tolil is dissolved by 30 cc. of boiling xylene, from which it separates in minute, yellow crystals.

Tetraiodophthal-*m*-tolil.—The preparation and yield of the *m*-tolil were the same as given for the *o*-tolil. The product melted at 325–326° (corr.) after three recrystallizations from xylene using boneblack. One gram dissolves in 30 cc. boiling xylene and crystallizes in fine, yellow blades.

Subst. (I) 0.2877, (II) 0.2678; cc. 0.1 *N* $AgNO_3$, (I) 15.66, (II) 14.56.
Calc. for $C_{15}H_7O_2NI_4$: I, 68.53. Found: (I) 69.08, (II) 69.01.

Tetraiodophthal-*p*-tolil.—Fifty grams of the anhydride were dissolved in 200 cc. of boiling nitrobenzene, 15 g. of *p*-toluidine added, and the boiling continued one minute. The product melted at 317–318° (corr.) after two recrystallizations from xylene using boneblack. One gram of the *p*-tolil is dissolved by 40 cc. of boiling xylene. It crystallizes in yellow blades.

Subst. (I) 0.2320, (II) 0.3743; cc. 0.1 *N* $AgNO_3$, (I) 12.78, (II) 20.39.
Calc. for $C_{15}H_7O_2NI_4$: I, 68.53. Found: (I) 69.91, (II) 69.14.

Tetraiodophthal-*m*-nitroanil.—This was prepared like the *o*-tolil. The yield was 29 g., 82%. A part of this was recrystallized twice from acetic acid, after which its melting point of 318–319° (corr.) was unchanged by another recrystallization.

Subst. (I) 0.2433, (II) 0.2504; cc. 0.1 *N* $AgNO_3$, (I) 12.69, (II) 13.10.
Calc. for $C_{14}H_4O_4N_2I_4$: I, 65.78. Found: (I) 66.20, (II) 65.95.

The *m*-nitroanil is soluble in about 1000 parts of boiling acetic acid from which it crystallizes in fine, yellow, matted needles. It is much more soluble in xylene and nitrobenzene but does not crystallize well from these solvents.

Under the conditions mentioned above, even on boiling considerably longer, *p*-nitraniline does not appear to react with tetraiodophthalic anhydride. The latter crystallizes out unchanged. *o*-Nitraniline acts only very slowly.

Tetraiodophthal-*p*-hydroxyanil.—This substance is decomposed by boiling nitrobenzene, so the following method was adopted: A boiling solution of 12 g. *p*-aminophenol in 1200 cc. of xylene was added to a boiling solution of 30 g. of the anhydride in 800 cc. of xylene. The purplish gray precipitate was filtered off, added to a liter of boiling acetic acid, boiled one minute, cooled and filtered. A portion melted at

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330–336° (corr.) (with decomposition), after recrystallization from about 4000 parts of acetic acid. It crystallizes in very fine, yellow needles almost insoluble in xylene, excessively soluble in pyridine.

Subst. (I) 0.2837, (II) 0.5972; cc. 0.1 *N* $AgNO_3$, (I) 15.14, (II) 31.94.
Calc. for $C_{14}H_8O_3NI_4$: I 66.79. Found: (I) 67.73, (II) 67.88.

Tetraiodophthal-*p*-acetylaminoanil.—Fifteen grams of *p*-aminoacetanilide were added to a boiling solution of 50 g. of the anhydride in 200 cc. of nitrobenzene. A part of the product was crystallized from nitrobenzene in minute, yellow blades of melting point 339° (corr.) (with decomposition), unchanged by a recrystallization from nitrobenzene.

Subst. (I) 0.4612, (II) 0.4873; cc. 0.1 *N* $AgNO_3$, (I) 22.79, (II) 24.19.
Calc. for $C_{16}H_8O_3N_2I_4$: I 64.77. Found: (I) 62.72, (II) 63.01.

The product is practically insoluble in xylene and acetic acid, somewhat soluble in phenol and pyridine. One gram dissolves in 400 cc. of boiling nitrobenzene.

Summary.

(1) The systematic study of phthalic acid derivatives from the standpoint of constitution and color has been continued by the preparation of a large number of derivatives of tetrachloro- and tetraiodophthalimides. New methods have been used for the preparation of these compounds which are improvements upon methods previously used for similar preparations.

(2) A study of the action of various amines on nuclear substituted phthalic anhydrides indicates that the first stage of this type of reaction is a molecular addition involving secondary valency forces only, and often resulting in the production of a deep red color. Tertiary amines show no further action on the anhydride ring; primary and secondary amines rapidly break it, forming the colorless amic acid or its salts.

(3) A new type of phthalic acid derivative has been prepared by replacing chlorine in the nucleus by anilino groups.

(4) The dimorphic modifications of tetrachlorophthal-*p*-tolil show a difference in color, melting point, and ability to combine with solvents.

(5) The spectroscopic study of halogenated phthalimide derivatives will be reported in a later paper.

PITTSBURGH, PA.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF PITTSBURGH.]

PHTHALIC ACID DERIVATIVES; CONSTITUTION AND COLOR, VI. THE ACTION OF AMINES UPON DICHLORO-PHTHALIC ANHYDRIDES.

BY DAVID S. PRATT AND GRANVILLE A. PERKINS.

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The action of amines on halogenated phthalimides and their derivatives first came to the authors' attention in connection with preparing tetra-

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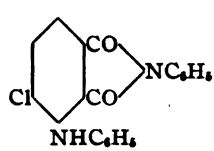
chlorophthalanil and similar compounds. When the aniline salt of tetrachlorophthalic acid is heated[1] it loses water and aniline, giving the anil. The product, however, is contaminated with deeply colored tarry impurities. Aniline 3,6-dichlorophthalate acts in the same way.[2] The formation of tarry by-products in preparing anils can be minimized by using the method of Tingle and Bates, that is, heating the phthalanilic acid in 50% alcohol; by the method of Graebe and Gourevitz,[3] which consists in heating the anhydride in aniline, or best by the method described in a previous article[4] namely, warming the anhydride with aniline in acetic acid solution. The last is a modification of Zincke & Cooksey's method[5] for phthalanil. For some reason, inexplicable to us, they considered it necessary to keep the temperature down. These three methods, with variations, were found to furnish means for the convenient preparation of a large number of halogenated phthalimide derivatives. This paper, however, deals with some of the tarry by-products mentioned above. We have ascertained that one of the effects of amines upon halogenated phthalimides is to replace one or more halogen atoms. For example the 3,6- and 3,4-dichlorophthalanils on long boiling in aniline give anilinochlorophthalanils. The 3,5-dichlorophthalic anhydride was not available for investigation; from the 4,5-derivative no anilino product was obtained.

Concerning the relative activity of α and β chlorine atoms toward aniline, nothing can be said at present except that the 4,5-dichlorophthalanil is relatively very inactive. This indicates that the α chlorine atom, not the β, in 3,4-dichlorophthalanil is replaced giving 3-anilino-4-chlorophthalanil.



The type of dimorphism existing between the two for ms of 3,4-dichlorophthalanil and of 3-anilino-6-chlorophthalanil has been discussed in connection with tetrachlorophthal-*p*-tolil[6] which exhibits the same peculiarity.

EXPERIMENTAL.

The Dichlorophthalic Acids.

The chlorination of phthalic anhydride was carried on in a similar manner to that described by Villiger[7] but since his manipulation is somewhat

[1] Graebe and Buenzod, *Ber.*, **32**, 1994 (1899).
[2] Tingle and Bates, THIS JOURNAL, **32**, 1324 (1910).
[3] *Ber.*, **33**, 2024 (1900).
[4] THIS JOURNAL, **40**, 198 (1918).
[5] *Ann.*, **255**, 375 (1889).
[6] THIS JOURNAL, **40**, 208 (1918).
[7] *Ber.*, **42**, 3538 (1909).

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difficult when working with large quantities in the laboratory, a simplification was adopted.

Fifteen hundred grams of phthalic anhydride, dissolved in an equal weight of 50% fuming sulfuric acid, were maintained at a temperature of 60–70° while a slow stream of chlorine was passed through for about 40 hours. Since sulfur oxides escaped it was impossible to control the operation by Villiger's method of weighing, and a crude test for sufficient chlorination was resorted to. A small sample was taken and boiled with four times its volume of water. When a few crystals remained undissolved, or when the solution on cooling and seeding with tetrachlorophthalic acid gave crystals within an hour, the chlorination was stopped.

The three dichloro anhydrides formed were separated by Villiger's method. The calcium precipitate weighed 974 g., indicating that 35% of the phthalic anhydride was chlorinated in the 3,6 positions. The zinc salt weighed 1746 g., indicating that 58% of the original anhydride had been changed to the 3,4 and 4,5 derivatives. The yields of pure anhydrides, however, were very poor compared to these figures especially in the case of the 3,4 and 4,5 anhydrides, which are difficult to separate. The melting points of the anhydrides obtained are as follows: (Villiger's figures in parentheses.)

3,4- 120–121° corr. (120–121°); 3,6- 193.5–194.5° corr. (190–191°); 4,5- 187.5–188° corr. (185–187°).

3,4-Dichlorophthalanil.—Forty grams of aniline were added to a boiling solution of 40 g. of 3,4-dichlorophthalic anhydride in 200 cc. of acetic acid. The product, 52 g., represented about 97% yield. This was filtered off after cooling and recrystallized from acetic acid and alcohol. The melting point of 181–181.5° corr. was unchanged by recrystallization from acetic acid. It was analysed by the lime combustion method.

Subst. (I) 0.1732 g., (II) 0.3026 g.; cc. 0.1 *N* $AgNO_3$, (I) 11.94, (II) 20.65.
Calc. for $C_{14}H_7O_2NCl_2$: Cl, 24.28. Found: (I) 24.45, (II) 24.21.

One gram of the anil dissolves in 3 cc. of boiling acetic acid, or nearly 100 cc. of boiling alcohol. It is soluble in ethyl acetate and benzene but does not crystallize as well from the latter.

Dimorphism.—3,4-Dichlorophthalanil usually crystallizes in silky needles with a pale yellow cast. This is the form described above, the melting point of which was taken by the usual method. The usual method, however, does not give the true melting point of this modification, for the powdered substance in the capillary tube changes readily on heating into a different and more stable form. One then observes the melting of this stable form. The true melting point of the needles was found by dipping samples of the fine crystals contained in capillary tubes into a bath at various known temperatures. When dipped into a bath at 172° (corr.) the needles did not melt, but immediately changed to a white powder.

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Immersed in a bath at 174° the crystals melted to a pasty condition. Fresh crystals at 178° melted more completely, those on the sides of the tube giving clear droplets which quickly clouded or solidified due to precipitation of the stable form. It is evident that the melting point of the needles is approximately 174° (corr.) but at this temperature fusion is not rapid enough to be complete before precipitation of the stable form sets in.

The stable modification was prepared by allowing the anil to stand several days in contact with acetic acid. The needles disappeared and compact *colorless* prisms were formed that melted at 182–182.5° (corr.). Neither modification contained solvent of crystallization.

3-Anilino-4-chlorophthalanil (4,3,?).—Twenty grams of 3,4-dichlorophthalic anhydride were boiled with 60 g. of aniline for 10 hours in an atmosphere of natural gas. Crystals of aniline hydrochloride were formed on cooling. After mixing with acetic acid the product was poured into dilute hydrochloric acid. The orange precipitate was recrystallized from alcohol using boneblack. Eighteen grams of orange crystals were thus obtained, which on two repetitions of the treatment gave 9 g. with a melting point of 159.5–160° (corr.) unchanged by recrystallization.

Subst. (I) 0.3681 g., (II) 0.4612 g.; cc. 0.1 *N* $AgNO_3$, (I) 10.72, (II) 13.35.
Calc. for $C_{22}H_{13}O_2N_2Cl$: Cl, 10.17. Found: (I) 10.33, (II) 10.26.

One gram of the anilino anil dissolves in 70 cc. of boiling alcohol crystallizing in orange leaflets. It is very soluble in acetic acid.

As an experiment on the further action of aniline, ten grams of 3,4-dichlorophthalic anhydride were boiled gently in aniline for 36 hours. The product was more contaminated by tarry material than before, but 5.5 grams melting at 158–159° were obtained and identified by a mixed melting point with the product from shorter boiling.

3,6-Dichlorophthalanil.—One hundred grams of 3,6-dichlorophthalic anhydride were dissolved in 500 cc. of boiling acetic acid, and 100 g. of aniline added. 110 g. representing an 82% yield, of light yellow blades separated on cooling. After recrystallization from acetic acid, the product had a melting point of 197–8° (corr.), unchanged by boiling with boneblack and recrystallization. Graebe and Gourevitz record a melting point of 191°; Tingle and Bates, 201°. One gram of the anil dissolves in 5 cc. of boiling acetic acid.

Subst. (I) 0.2038, (II) 0.2942; cc. 0.1 *N* $AgNO_3$, (I) 14.05, (II) 20.19.
Calc. for $C_{14}H_7O_2NCl_2$: Cl, 24.28. Found: (I) 24.45, (II) 24.34.

3-Anilino-6-chlorophthalanil.—Twenty grams of 3,6-dichlorophthalic anhydride were boiled with 70 cc. of aniline in an atmosphere of natural gas for about 24 hours. (Short heating was found insufficient.) The product was mixed with acetic acid and poured into dilute hydrochloric acid. The dried precipitate, which weighed 33 g., was recrystallized from acetic acid and twice from alcohol using boneblack. One gram of the

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substance dissolves in 9 cc. of boiling acetic acid or 110 cc. of boiling alcohol.

Subst. (I) 0.3489 g., (II) 0.4114 g.; cc. 0.1 *N* $AgNO_3$, (I) 10.23, (II) 12.03.
Calc. for $C_{20}H_{12}O_2N_2Cl$: Cl, 10.17. Found: (I) 10.40, (II) 10.37.

Dimorphism.—3-Anilino-6-chlorophthalanil, when crystallized from alcohol was usually obtained in the unstable form of orange needle-like blades, melting at about 141° (corr.) to a clear liquid which quickly solidified. This melting point was determined as in the case of 3,4-dichlorophthalanil. The usual method of slow heating changes the substance to the stable form so that the observed melting point is very close to 160°. Fairly rapid heating, however, causes the powdered crystals to melt or soften at about 141°.

The stable form of small orange prisms may be obtained by letting the blade-like crystals stand in contact with solvent, or by heating them with or without solvent. The change on heating takes place without change in weight, showing that solvent of crystallization is not involved. The prisms melt at 160–160.5° (corr.) Although there was hardly a possibility that the substance could be the same as that obtained from 3,4-dichlorophthalanil, still, in view of the almost identical melting points, the distinction was established by a mixed melting point.

4,5-Dichlorophthalanil.—To a boiling solution of twenty grams of 4,5-dichlorophthalic anhydride in 120 cc. of acetic acid, 20 g. of aniline were added. The product, weighing 22 g., representing 82% yield, was filtered off after cooling and crystallized three times from acetic acid using bone-black. Its melting point of 212.5–213° (corr.) was unchanged by recrystallization.

Subst. (I) 0.3062 g., (II) 0.2714 g.; cc. 0.1 *N* $AgNO_3$, (I) 21.09, (II) 18.76.
Calc. for $C_{14}H_7O_2NCl_2$: Cl, 24.28. Found: (I) 24.42, (II) 24.51.

One gram of the anil dissolves in 15 cc. of boiling acetic acid, from which it crystallizes in colorless rhombic leaflets. Occasionally needles are formed especially from slightly impure solutions. This modification was very unstable and was not further investigated.

Attempts to displace the chlorine by means of aniline were unsuccessful, as the anil was attacked only very slightly on boiling for 48 hours. Extremely long boiling gave nothing but tarry products.

Summary.

(I) The 3,4- and 4,5-dichlorophthalanils have been prepared, and the method applied also in obtaining 3,6-dichlorophthalanil.

(II) The action of boiling aniline on the 3,4- or 3,6-dichlorophthalanils, replaces a chlorine atom by the anilino group, but the 4,5-isomer is relatively inactive.

(III) 3,4-Dichlorophthalanil and 3-anilino-6-chlorophthalanil exhibit dimorphism.

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(IV) A study of the spectroscopic relations of the dichlorophthalic acids will be made in the near future.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF PITTSBURGH.]

PHTHALIC ACID DERIVATIVES; CONSTITUTION AND COLOR, VII. DIIODO-, TRIIODO-, AND DICHLORODI-IODOPHTHALIC ACIDS.

BY DAVID S. PRATT AND GRANVILLE A. PERKINS.

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The replacement of chlorine in halogenated phthalanils[1] by the anilino group results in a new and interesting type of phthalic acid derivatives, but the reaction is slow and the yields not always good. One of the reasons for preparing the diiodophthalic acids was to experiment on the corresponding replacement of iodine by anilino groups. It was expected that iodine would act more smoothly than chlorine in such a replacement. It was found to act readily enough, but unfortunately tarry products were formed from which no pure substances could be isolated.

The value of the iodophthalic acids as intermediate steps in the preparation of hydroxyphthalic acids will be taken up in connection with establishing their structures, and the spectroscopic relations of these acids to other phthalic derivatives will be discussed in a later paper.

Practically no information could be found in the literature concerning the diiodo, and nothing at all concerning triiodo and dichlorodiiodophthalic acids. Edinger and Goldberg[2] prepared a diiodophthalic acid from 4, iodo-*o*-xylene, and recorded a melting point of 195°, which is about ten degrees lower than what we find for 3,4-diiodophthalic acid, but this is probably the isomer they had.

The partial iodination of phthalic acid was carried out in 50% fuming sulfuric acid, the two methods of treatment employed being long heating at 75°, and rapid heating to 200°. The first gave nearly equal amounts of 3,4- and 3,6-acids, and much smaller amounts of 4,5- and triiodo anhydride. Rapid heating gave the same amount of 4,5- with a larger amount of 3,4- and triiodo anhydride at the expense of the 3,6-. Compared with the action of chlorine on phthalic anhydride,[3] the difference indicated a greater tendency toward the 3,4-positions. The formation of a tri-substitution product was not observed in using chlorine. Although the yield of the 4,5-derivative is small in both chlorination and iodination, it is interesting to note that the only product so far isolated from the mixture obtained by partial bromination is 4,5-dibromophthalic anhydride.[4]

[1] Cf. two preceding papers.

[2] *Ber.*, **33**, 2880 (1900).

[3] V. Villiger, *Ber.*, **42**, 3530 (1909).

[4] Lesser and Weiss, *Ber.*, **46**, 3937 (1913). But cf. *Ibid.*, p. 3944.

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Separation.

The separation of the diiodophthalic acids by the method Villiger used for the dichlorophthalic acids was not found feasible because the zinc salts of all the former acids proved to be insoluble. A partial separation was accomplished by esterification, since only the 4,5- and a part of the 3,4-acid formed neutral esters.

The esterification was effected at room temperature by alcohol saturated with hydrochloric acid. After two days the mixture was treated with a slight excess of dilute sodium hydroxide and the neutral esters extracted with ether. From the ether extract, after saponification by a mixture of sulfuric and acetic acids, a small amount of 4,5-diiodophthalic acid was isolated. The alkaline solution remaining after extraction with ether slowly deposited crystals of nearly pure sodium ethyl 3,4,6-triiodophthalate. Treatment of this salt with hydrochloric acid gave the acid ester, from which pure 3,4,6-triiodophthalic anhydride was obtained by boiling with acetic acid. A complete separation on these principles was not attempted since much better methods were soon available.

It was found that the 3,4- and 4,5-acids crystallize from 95% acetic acid without losing water while the 3,6- and triiodo acids are converted into anhydrides that can then be separated from the above acids by their much greater solubility in benzene. The 3,4- and 4,5- pair were then separated by repeated crystallization from acetic acid. The latter acid goes into solution in boiling acetic acid much more quickly and crystallizes out more readily than the 3,4-isomer.

It was finally found that an easy separation of all four acids can be effected by combining the two principles:

(1) When fractionally precipitated from a solution of their di-sodium salts by acetic acid the order of deposition of the mono-sodium salts is as follows: 4,5-salt, triiodo salt, and 3,4-salt; the 3,6-salt remaining in solution.

(2) The 3,6- and triiodo acids readily lose water giving anhydrides which can then be extracted by benzene.

Structure.

The positions of iodine atoms in the products obtained by iodination of phthalic anhydride were determined by hydrolysis. This was effected by boiling in strong sodium hydroxide solution, but the yields were not good, due to various side reactions. Curiously enough, the most troublesome of these side reactions was *reduction*, which occurred in the case of 3,6-diiodophthalic acid, the final result being 3-hydroxyphthalic acid. Apparently the cause of reduction was the simultaneous oxidation of a part of the product in the presence of strong alkali. Not only was 3-hydroxyphthalic acid an unexpected product, but its identification was attended with some difficulty at first due to incorrect melting points recorded in the

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literature for its anhydride. The uncertainty was removed, however, by titration of a number of its derivatives and by a mixed melting point with some known 3-hydroxyphthalic anhydride prepared from 3-nitrophthalic acid.

Since 3,6-diiodophthalic acid could not be directly hydrolyzed to 3,6-dihydroxyphthalic acid, it was hydrolyzed in two steps. Replacement of one iodine atom by hydroxyl was readily affected by silver sulfate in aqueous pyridine solution, of the second by 1:1 sodium hydroxide. Since the final result was 3,6-dihydroxyphthalic acid the acid in question is 3,6-diiodophthalic acid.

Another of our diiodophthalic acids yielded, on treatment with sodium hydroxide, 4,5-dihydroxyphthalic acid and a second substance probably 3,4,5-trihydroxyphthalic acid. It is therefore 4,5-diiodophthalic acid.

Another diiodophthalic acid yielded 3,4-dihydroxybenzoic acid, thus showing that the iodine atoms in it also are *ortho* to each other. It is therefore 3,4-diiodophthalic acid.

The triiodophthalic acid yielded 3,6-dihydroxyphthalic and probably some 3,5-dihydroxybenzoic. It is therefore 3,4,6-triiodophthalic acid.

Iodination of the Dichlorophthalic Anhydrides.

The introduction of iodine into the dichlorophthalic anhydrides took place smoothly except in the case of the 3,6-isomers. Even at a comparatively low temperature this anhydride yielded considerable tetraiodophthalic anhydride. This contamination was easily removed by hydrating the chlorinated product and extracting the unchanged tetraiodophthalic anhydride with benzene.

One of the reasons for preparing the dichlorodiiodophthalic acids was to prepare if possible from them dianilinodichlorophthalanils of known structure. It was hoped that the structure of the dianilino product from tetrachlorophthalanil could then be established by identifying it with one of these. The replacement of iodine by the anilino group, however, was found to be difficult (cf. diiodophthalic acids above) and we succeeded only in obtaining a small amount of impure 3,6-dianilino-4,5-dichlorophthalanil. This was found to be different from the previously obtained isomer, but further investigation will be necessary to decide the structure of the latter.

Experimental.

Iodination of Phthalic Anhydride.—A mixture of 74 g. of phthalic anhydride, 127 g. (two atomic equivalents), of iodine, and 250 g. of 50% fuming sulfuric acid, was placed in an oil bath heated to approximately the following temperatures: 110–120° for 1.5 hrs.; 140–160° for 1 hr.; 160–200° for 15 minutes; and 200° for 5 minutes. A brisk evolution of sulfur dioxide took place during most of this time. The hot mixture was poured into a porcelain dish and exposed to the air several hours. Two

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hundred and fifty grams of ice were then added with thorough stirring. The precipitate was filtered off, washed with 100 cc. of cold water, and dissolved in 250 cc. of warm 20% sodium hydroxide solution, avoiding unnecessary heating. The solution after filtering off a slight precipitate of ferric oxide and neutralizing with acetic acid, measured about 450 cc.

The neutral solution of sodium salts was then fractionally precipitated by successive additions of acid, warming after each addition and stirring for 2 hours as it cooled. 10 cc. of acetic acid gave a precipitate of 16 g. 5 cc. of acetic acid then gave a precipitate of 1 g. Both of these precipitates were found to be nearly pure mono-sodium 4,5-diiodophthalate. 10 cc. of acetic acid then gave 31 g., chiefly mono-sodium 3,4,6-triiodophthalate. Twenty cc. of hydrochloric acid then gave 91.5 g., chiefly mono-sodium 3,4-diiodophthalate. The solution was then treated with a large excess of hydrochloric acid and heated several hours in a water oven. The precipitate of 47 g. was chiefly 3,6-diiodophthalic anhydride.

The first two precipitates were treated according to the following general method: Five parts of the impure mono-sodium 4,5-diiodophthalate were dissolved in 50 parts of a hot 10% sodium acetate solution with the aid of a very slight excess of sodium hydroxide. The solution was made neutral to litmus with acetic acid and then one part of the acid added in excess. The solution was allowed to stand several hours before the crystals which formed were filtered off. In this case the mother liquor was added to the triiodo fraction, since it contained some of the triiodo and 3,4-acid. When much triiodo or 3,4-acid was present both the amount of acetic acid and the time allowed for crystallization were reduced. The pure crystals were converted into acid by dissolving in hot dilute sodium hydroxide and precipitating with excess hydrochloric acid.

The third and fourth fractions were separately dissolved in dilute sodium hydroxide and precipitated by a large excess of hydrochloric acid. Heating for several hours seems to be necessary for complete precipitation, especially of the 3,6-acid, which is thereby converted into its anhydride.

The next step was to extract each of the fractions with boiling benzene. The extracts from the third and fifth contained nearly pure triiodo- and 3,6-diiodophthalic anhydrides respectively, and the residue from the fourth contained nearly pure 3,4-diiodophthalic acid.

Although at this point a large part of the iodination product had been separated into its constituents, further quantities were recovered as follows. The residue from the benzene extraction of the third fraction was separated into 3,4- and 4,5-acids by recrystallizing the sodium salts as above described. The benzene extract from the fourth fraction was separated by the same method into mono-sodium triiodophthalate (crystals) and the 3,6-salt (filtrate). Here much more acetic acid may be used, and sodium acetate is unnecessary.

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Effect of Temperature.

Phthalic anhydride was again iodinated, using the same quantities as before, but changing the manner of heating. The mixture was kept at about 75° for six days. The anhydrides were precipitated as before but it was found necessary to wash them with sodium sulfite solution to remove a little free iodine still remaining. The separation was carried out practically as before, but different yields of the various anhydrides were obtained. The results of the two methods of heating are compared in the following table. The first two columns show the amounts of fairly pure acids or anhydrides obtained by the process of separation described. The last two columns are calculated from the first two and show what fraction of the original phthalic anhydride each weight represents.

	Low temperature. G.	High temperature. G.	Low temperature. Per cent.	High temperature. Per cent.
3,6-Anhydride	56.5	34.5	28.3	17.3
3,4-Acid	52.5	62.5	25.1	29.9
4,5-Acid	16.0	16.5	7.6	7.9
3,4,6-Anhydride	20.0	34.0	7.6	12.9
Total			68.6	68.0

Only traces of tetraiodophthalic anhydride were formed in the above-mentioned iodinations and several others similarly carried out. The insolubility of its mono-sodium salt sometimes caused it to precipitate with the triiodophthalic fraction, but it generally remained in supersaturated solution until the precipitation of the 3,6-diiodophthalic anhydride. Traces of 4-iodophthalic acid were also found. This substance was isolated from the filtrates resulting in the course of the above-described separation from the precipitation of the diiodophthalic acids with hydrochloric acid. The combined filtrates from a mixture prepared just as stated in the first paragraph, *i. e.*, an iodination at the higher temperatures, were extracted with ether.

The extract, weighing fifteen grams, was dissolved in dilute sodium hydroxide and subjected to fractional precipitation by acetic acid. The first fraction contained mono-sodium 4,5-diiodophthalate, and the last fraction mono-sodium 4-iodophthalate. The acid was freed by strong hydrochloric acid, and converted into anhydride by warming with a small amount of acetic anhydride. The mixture was dissolved in boiling ligroin from which about 0.5 g. of nearly colorless leaflets were deposited on cooling, melting at 124° (corr.). This substance was evidently 4-iodophthalic anhydride, for which a melting point of 123° is recorded.[1]

3,4-Diiodophthalic Acid.—The pure acid was obtained by dissolving the anhydride in warm sodium hydroxide solution, diluting with boiling water,

[1] Edinger, *J. prakt. Chem.*, [2] 53, 387 (1896).

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and acidifying with excess of hydrochloric acid. Colorless leaflets were formed which melted at 212–213° corr. (giving off water), on rapid heating. They were air dried and titrated with standard sodium hydroxide using phenolphthalein and boiling to remove CO_2.

Subst. (I) 0.2154, (II) 0.2252; cc. 0.1 *N* NaOH, (I) 10.34, (II) 10.80.
Calc. for $C_8H_4O_4I_2$: Molecular weight, 417.9. Found: (I) 416.7, (II) 417.0.

3,4-Diiodophthalic acid is slightly soluble in water. When in the crystalline condition it is only slightly soluble in ether, very soluble when amorphous. One gram dissolves in about 8 cc. of acetic acid on long boiling and crystallizes very slowly after cooling, in warty aggregates. It is partly converted into anhydride by the concentration of its solution in glacial acetic acid.

Mono-sodium 3,4-diiodophthalate is much more soluble than the corresponding salt of the 4,5-isomer or of 3,4,6-triiodophthalic acid. The addition of sufficient sodium acetate to a solution of the disodium salt of the 3,4-acid entirely prevents precipitation by any amount of acetic acid.

3,4-Diiodophthalic Anhydride.—The "nearly pure" 3,4-acid separated from its isomers as above described, was heated with benzene containing acetic anhydride. The product was then recrystallized several times, using boneblack, from benzene containing a slight addition of acetic anhydride. It crystallizes in almost colorless prisms with a fibrous fracture, melting at 198–198.5° (corr.).

Subst. (I) 0.3558, (II) 0.4171; cc. 0.1 *N* $AgNO_3$, (I) 17.86, (II) 20.89.
Calc. for $C_8H_2O_3I_2$: I, 63.48. Found: (I) 63.71, (II) 63.57.[1]

Hydrolysis of 3,4-Diiodophthalic Acid.—Fifty grams of 3,4-diiodophthalic acid and 50 g. of sodium hydroxide were added to 350 cc. of water and the solution boiled for 8 hrs. in an atmosphere of natural gas. During this time gradual concentration to 100 cc. was effected. The solution was then strongly acidified with hydrochloric acid and extracted with ether. The ether extract was recrystallized from hydrochloric acid giving 3 g. of product. This was recrystallized from water, melting then at 198–200° (corr.) with evolution of gas. Since its aqueous solution gave a bluish green with ferric chloride that was changed to violet and then red by dilute sodium carbonate the substance was evidently 3,4-dihydroxybenzoic acid, the melting point of which is recorded as 199° with decomposition.[2]

As an additional proof of its identity, the 3,4-dihydroxybenzoic acid

[1] In this and subsequent iodine determinations the lime combustion method was used, but a slight excess of the standard silver nitrate solution was added before acidification. This prevented the loss of iodine, which otherwise occurred so easily when the nitric acid was added, and the heat of neutralization effected a rapid solution of both lime and silver oxide. Sodium sulfite was added after filtration, to reduce any silver iodate formed and precipitate it as iodide.

[2] Mulliken, "The Identification of Pure Organic Compounds," 1, 50.

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was esterified with ethyl alcohol containing hydrochloric acid. The ester melted at 132–135° (corr.) Fittig and Macalpine record 133–134°.[1]

3,4-Diiodophthalanil.—Five parts of 3,4-diiodophthalic anhydride were dissolved in about 65 parts of boiling acetic acid, and 2 parts of aniline added. The yield on cooling was the same as the original weight of anhydride, *i. e.*, 84% theoretical. It was recrystallized twice from xylene, having then a melting point of 270–271° (corr.) unchanged by another crystallization. One gram dissolves in 15 cc. of boiling xylene from which it crystallizes in very pale yellow prisms.

Subst. (I) 0.4448, (II) 0.3555; cc. 0.1 *N* $AgNO_3$, (I) 18.75, (II) 15.07.
Calc. for $C_{14}H_7O_2NI_2$: I, 53.44. Found: (I) 53.50, (II) 53.80.

3,6-Diiodophthalic Acid.—3,6-Diiodophthalic anhydride (see below) was dissolved in dilute sodium hydroxide and hydrochloric acid added to the cooled solution. Colorless leaflets of the corresponding acid were obtained. This substance loses water slowly at 100°, and is converted to the anhydride below its melting point when rapidly heated in a capillary tube.

Titration of the acid is rendered difficult by the action of boiling water upon it. The iodine is apparently attacked in neutral, slightly acid, or alkaline solution, with the result that too much alkali is taken up unless the period of boiling to effect solution and remove carbon dioxide is very brief. An air-dried sample was titrated as rapidly as possible with standard hydroxide.

Subst. (I) 0.1374, (II) 0.0847; cc. 0.1 *N* NaOH, (I) 6.56, (II) 4.06.
Calc. for $C_8H_4O_4I_2$: Molecular weight, 417.9. Found: (I) 418.9, (II) 416.9.

3,6-Diiodophthalic acid forms a very soluble mono-sodium salt. A saturated solution of the di-sodium salt gives no precipitate on addition of acetic acid. This behavior affords a nearly complete separation from the products which accompany it in its preparation from phthalic acid.

3,6-Diiodophthalic Anhydride.—The benzene extract containing this substance (see page 222), was treated with a little acetic anhydride, to dehydrate the traces of 3,4- and 4,5- acids present, and then concentrated. The yellow prisms obtained were crystallized several times from benzene, using boneblack, giving a nearly colorless product melting at 234.5–235.5° (corr.).

Subst. (I) 0.3768, (II) 0.4189; cc. 0.1 *N* $AgNO_3$, (I) 18.92, (II) 20.89.
Calc. for $C_8H_2O_3NI_2$: I, 63.48. Found: (I) 63.73, (II) 63.29.

Hydrolysis of 3,6-Diiodophthalic Acid.—The iodine in 3,6-diiodophthalic acid is readily attacked by hydrolyzing agents but in most cases the isolation of pure products is difficult. A nearly neutral solution of the di-sodium salt or a solution of the acid sodium salt slowly becomes more acidic on boiling, showing that hydrolysis of the iodine takes place even

[1] *Ann.*, **168**, 114 (1873).

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in neutral or acid solution. At the same time a reddish brown color developes. Boiling in alkaline solution effects a somewhat more rapid hydrolysis, and less color is developed. Many hours, however, were found to be required for complete hydrolysis using 10% sodium hydroxide and the only product isolated was 3-hydroxyphthalic acid, (see below). This was contaminated with large amounts of tarry matter, which was perhaps produced by the oxidation of some of the 3,6-dihydroxyphthalic acid first formed while the remainder of the dihydroxy acid was reduced. The result of shortening the time of boiling to about 3 hours was that the yield of 3-hydroxyphthalic acid was less, but no 3,6-dihydroxy acid could be isolated.

Attempts to use much stronger alkali failed, due to the insolubility of the salts of 3,6-diiodophthalic acid in strong alkalies. Fusion with potassium or sodium hydroxides resulted in charring. In contrast to this behavior, it was found that 3-hydroxy-6-iodophthalic acid could readily be hydrolyzed by 1:1 sodium hydroxide. One of the differences is the greater solubility of the salts of the partially hydrolyzed acid.

The Action of Silver Salts in Pyridine Solution on Iodinated Phthalic Acids.—The partial hydrolysis of 3,6-diiodophthalic acid was easily accomplished by the use of silver salts in pyridine solution. The sulfate was preferred to the nitrate as it gives no oxidizing agent upon acidification.

Since silver salts in pyridine reacted so smoothly with 3,6-diiodophthalic acid a few experiments were made upon other halogenated phthalic acids. The silver sufate reagent (described below) quickly gave silver iodide with tetraiodophthalic anhydride, but the 3,4-diiodo derivative required a more concentrated reagent, either silver nitrate or benzoate dissolved in a very little pyridine. These salts remain fused when almost all of the pyridine has been distilled off, and produce a more energetic action than the sulfate whose solution cannot be made so concentrated. The fused nitrate, however, has the disadvantage of causing explosions.

4,5-Diiodo- and tetrachlorophthalic anhydrides gave almost no silver halide even with the concentrated nitrate reagent.

3-Hydroxy-6-iodophthalic acid was found to be very slowly affected by the concentrated benzoate reagent.

3-Hydroxy-6-iodophthalic Anhydride Acetate.—Five grams of 3,6-diiodophthalic anhydride, and 10 g. of silver sulfate were added to a mixture of 25 cc. of pyridine and 2 cc. of water. The solution was boiled in an atmosphere of natural gas for 1.5 hours. The silver iodide formed remained in solution, only a negligible precipitation perhaps of silver taking place. The golden brown solution was poured slowly into concentrated hydrochloric acid with a constant stirring and cooling. The precipitate of silver chloride and iodide was filtered off and washed with a little water. The filtrate and washings were extracted twice with ether,

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from which 3 g. of nearly colorless 3-hydroxy-6-iodophthalic acid crystallized on evaporation.

For complete purification the dried acid was warmed for 15 minutes with 5 cc. of acetic anhydride. 50 cc. of mixed xylene and ligroin were added, and the solution boiled a short time with boneblack. Two and one-half grams of slightly brownish square crystals were obtained which after two recrystallizations from the same solvent, melted at 148.5–152.5° (corr.).

Samples were titrated with sodium hydroxide, boiling to complete saponification.

Subst. (I) 0.1030, (II) 0.1008; cc. 0.1 *N* NaOH, (I) 9.43, (II) 9.20.
Calc. for $C_{10}H_8O_5I$: Molecular weight, 332.0. Found: (I) 327.7, (II) 328.5.

A dilute solution of 3-hydroxy-6-iodophthalic acid or its acetate gives with very little ferric chloride a blue-violet color changed by more ferric chloride through violet to a red which is destroyed only by a very large excess of the reagent.

3,6-Dihydroxyphthalic Acid.—Ten grams of 3-hydroxy-6-iodophthalic acid were ground in a mortar with 10 g. of pure sodium hydroxide and the mixture added to 100 cc. of 1:1 sodium hydroxide solution in a porcelain dish. The whole was heated rapidly to boiling with constant stirring, and then boiled vigorously for five minutes. A sample was acidified, extracted with ether, and an aqueous solution of the extract tested with ferric chloride. The colors, blue-violet changing to amber with excess, indicated that the second iodine atom had been removed and nearly pure 3-6-dihydroxyphthalic acid[1] was present.

Accordingly the whole product was acidified with hydrochloric acid, extracted with ether, and recrystallized from this solvent. A sample of the nearly colorless product was purified in the form of its acetate by boiling with acetic anhydride and adding boiling ligroin. A mixed melting point with 3,6-dihydroxyphthalic anhydride diacetate previously obtained (*loc. cit.*) was taken and the two samples found to be identical. Thus the position of the iodine atoms in 3,6-diiodophthalic acid was established.

3-Hydroxyphthalic Anhydride.—Fifty grams of 3,6-diiodophthalic anhydride and 50 g. of sodium hydroxide were dissolved in 700 cc. of water. The solution was boiled 20 hours in an atmosphere of natural gas during which it was concentrated to 100 cc. A large excess of hydrochloric acid was then added and the solution extracted with ether. After evaporation of the ether the product was recrystallized from hydrochloric acid and then boiled with 200 cc. of xylene, concentrating to 150 cc. The 3-hydroxyphthalic acid was thus converted to anhydride, which crystallized out on cooling. After two more crystallizations from xylene 5.5 g. of orange-yellow crystals were obtained melting at 198–199° (corr.). This

[1] See page 226.

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product was titrated with standard sodium hydroxide using phenolphthalein and boiling to remove CO_2.

Subst. (I) 0.1777, (II) 0.0763; cc. 0.1 *N* NaOH, (I) 21.51, (II) 9.23.
Calc. for $C_8H_4O_4$: Molecular weight, 164.1. Found: (I) 165.2, (II) 165.3.

No recorded melting point of pure 3-hydroxyphthalic anhydride could be found. Jacobsen gives 145–148°[1] and Bentley, Robinson and Weizman[2] 150–190° for samples admitted to be impure. Therefore a sample known to be 3-hydroxyphthalic anhydride was prepared from 3-nitrophthalic acid. The crude 3-hydroxyphthalic acid, prepared as described by Bernthsen[3] was converted to anhydride by boiling with xylene, crystallized from anhydrous ether to remove amorphous by-products and recrystallized from xylene. A small yield of brownish yellow crystals were obtained, melting at 198–199° (corr.). Mixed with the anhydride previously obtained it had the same melting point, thus showing the identity of the two samples. Since a dihydroxy, not monohydroxy derivative was desired, the hydrolysis was repeated in the manner described for triiodophthalic acid, but nothing except 3-hydroxyphthalic could be isolated.

3-Hydroxyphthalic Acid.—One gram of the 3-hydroxyphthalic anhydride was dissolved in 2 cc. of boiling water. Colorless prisms were formed on cooling which melted at about 161–163° (corr.) (with evolution of gas) on rapid heating. The melting point varies with the manner of heating. On very slow heating, crystals of the anhydride were formed, which then melted at about 194° (corr.).

Subst. (I) 0.0778, (II) 0.0709; cc. 0.1 *N* NaOH, (I) 8.54, (II) 7.87.
Calc. for $C_8H_6O_4$: Molecular weight, 182.1. Found: (I) 182.2, (II) 18c.2.

3-Hydroxyphthalic Anhydride Acetate.—One gram of 3-hydroxyphthalic anhydride (obtained from 3,6-diiodophthalic acid) was heated with 10 cc. of acetic anhydride for an hour, most of the solvent evaporating. 50 cc. of ligroin were added, and the solution boiled with boneblack. On further recrystallization from ligroin, using boneblack, 0.9 g. of colorless leaflets were obtained, melting at 113.5–115.5° corr. Titration of the acetate hydrolyzed it rapidly and completely.

Subst. (I) 0.0509, (II) 0.0964; cc. 0.1 *N* NaOH, (I) 7.37, (II) 13.99.
Calc. for $C_{10}H_6O_5$: Molecular weight, 206.1. Found: (I) 207.1, (II) 206.7.

3-Hydroxyphthalic Anhydride Benzoate.—Half a gram of 3-hydroxyphthalic anhydride was dissolved in 5 cc. of benzoyl chloride, warmed for an hour and the product crystallized from boiling ligroin without first removing the excess of benzoyl chloride. On recrystallization from the same solvent 0.6 g. of minute colorless crystals were obtained melting at 147.5–

[1] *Ber.*, **16**, 1965 (1883).
[2] *J. Chem. Soc.*, **91**, 111–112 (1907).
[3] *Ber.*, **19**, 166 (1866); cf. Kenner and Mathews, *J. Chem. Soc.*, **105**, 2478 (1914).

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148° (corr.). The benzoate appears to crystallize also in colorless leaflets, but dimorphism was not definitely established.

This product hydrolyzed on titration even in the cold, but more slowly than the acetate. The hydrolysis was easily completed by boiling.

Subst. (I) 0.0661, (II) 0.0737; cc. 0.1 *N* NaOH, (I) 7.40, (II) 8.01.
Calc. for $C_{16}H_8O_6$: Molecular weight, 268.1. Found: (I) 268.1, (II) 276.2.

The second sample was first titrated in the cold but it was not found possible to effect complete solution without some hydrolysis. 6.46 cc. 0.1 *N* were required, representing a molecular weight of 228. The hydrolysis was then completed by adding more sodium hydroxide and boiling. The final result is recorded above.

3,6-Diiodophthalanil.—Eighty grams of 3,6-diiodophthalic anhydride dissolved in about a liter of boiling acetic acid were treated with 40 g. of aniline. After boiling a minute the solution was allowed to cool. The product, 82 g., an 86% yield, was twice recrystallized from xylene, having then a melting point of 233.5–234° (corr.) unchanged by another crystallization.

Subst. (I) 0.3402, (II) 0.3806; cc. 0.1 *N* $AgNO_3$, (I) 14.35, (II) 16.05.
Calc. for $C_{14}H_7O_2NI_2$: I, 53.44. Found: (I) 53.54, (II) 53.52.

3,6-diiodophthalanil crystallizes in colorless rectangular plates, 1 g. of which is dissolved by 7 cc. of boiling xylene.

On heating the anil in excess of aniline 20 hours at 140° a deep red color was produced but only unchanged anil could be isolated. The anilino derivative was not obtained.

4,5-Diiodophthalic Acid.—The acid obtained as previously described was purified by recrystallization from glacial acetic acid, in which it is quite soluble and from which it always separated in the form of colorless needles. These effloresce on exposure to air, probably losing acetic acid of crystallization. From acetic acid containing some water leaflets are often formed. The acid is slightly soluble in hot water from which it crystallizes in needles or leaflets. The leaflets are the stable form at room temperature but the needles require long standing in contact with water before conversion to leaflets is complete. A sample of the *leaflets* prepared in this way, melted at 221–222° (corr.) on rapid heating, giving off water and forming the anhydride. The sample was analyzed by titrating with sodium hydroxide to determine its molecular weight.

Subst. (I) 0.2029, (II) 0.1998; cc. 0.1 *N* NaOH, (I) 9.71, (II) 9.57.
Calc. for $C_8H_4O_4I_2$: Molecular weight, 417.9. Found: (I) 417.8, (II) 418.4.

4,5-Diiodophthalic acid both dissolves in acetic acid and crystallizes out on cooling much more rapidly than the 3,4-isomer. The acid is almost insoluble in boiling benzene and its mono-sodium salt is very slightly soluble in water. All of these facts were of assistance in separating the 4,5-acid from its concomitants.

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4,5-Diiodophthalic Anhydride.—4,5-Diiodophthalic acid obtained as described on page 229, was dehydrated with acetic anhydride, using acetic acid or benzene as solvent. It was obtained from either of these in poorly formed prisms which became nearly colorless after several recrystallizations and melted at 216.5–217° (corr.). It is fairly soluble in hot benzene, less so in acetic acid.

Subst. (I) 0.2759, (II) 0.4241; cc. 0.1 *N* $AgNO_3$. (I) 13.85, (II) 21.26.
Calc. for $C_8H_2O_3I_2$: I, 63.48. Found: (I) 63.71, (II) 63.62.

Hydrolysis of 4,5-Diiodophthalic Acid.—Twenty-five grams of 4,5-diiodophthalic anhydride, and 25 g. of sodium hydroxide were dissolved in 200 cc. of water and boiled in an atmosphere of natural gas for 18 hours, concentrating to about 50 cc.

The solution was strongly acidified with concentrated hydrochloric acid and thoroughly extracted with ether. The ether extract was crystallized from concentrated hydrochloric acid, yielding 10 g. of light brown product which melted at 137–47°. On recrystallization from dilute hydrochloric acid using boneblack, the melting point was raised to 148–9°. The product was a mixture of two substances, one of which was extracted by a liter of boiling xylene in several portions. The xylene extract was recrystallized from the same solvent, giving 1 g. of silvery leaflets with a slight brownish cast. They melted at 250.5–252.5° (corr.). The colors which ferric chloride gave with an aqueous solution of the substance were almost exactly the same as those obtained with protocatechuic acid although varying more with conditions. The product was therefore 4,5-dihydroxyphthalic anhydride, for which a melting point of 247–248°[1] is recorded, and with which ferric chloride gives the same colors[2] as with protocatechuic acid.

To demonstrate further the identity of the substance it was treated with ethyl alcohol containing hydrochloric acid. The resulting diethyl 4,5-dihydroxyphthalate crystallized from water in colorless blades melting at 148.5–150° (corr.) Rossin records 152°.[3]

The hydrolysis product from 4,5-diiodophthalic acid which was not dissolved by boiling xylene was recrystallized from water, yielding about 0.5 g. of slightly brownish crystals which did not contain halogen, and melted slowly with decomposition, beginning at about 280° (corr.). It gave a greenish blue with a little ferric chloride and a yellow-green with excess. It was probably 3,4,5-trihydroxyphthalic acid for which Senhofer and Brunner[4] give a melting point of "over 270°, with evolution of CO_2." These authors state that ferric chloride when very dilute gives a violet, when concentrated a greenish brown color.

[1] Freund, *Ann.*, **271**, 385 (1892).
[2] *Loc. cit.*
[3] *Monatshef. Chem.*, **12**, 493 (1891).
[4] *Ibid.*, **1**, 474 (1880).

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4,5-Diiodophthalanil.—The use of 4,5-diiodophthalic acid for this preparation was attempted, since it happened that not much of the corresponding anhydride was at hand. The 4,5-acid was dissolved in acetic acid and acetic anhydride added. The solution was then treated with aniline, but the resulting crystals consisted of a mixture. On boiling in aniline, however, they gave off water and yielded nearly pure anil. This was recrystallized three times from xylene using boneblack, then having a melting point of 241.5–243° (corr.), unchanged by recrystallization from xylene and acetic acid. The reason for the last crystallization was a softening noticed at about 231° especially on rapid heating. This is not due to impurity, however, or solvent of crystallization but to the dimorphism, as explained below.

Subst. (I) 0.3344, (II) 0.4041; cc. 0.1 *N* $AgNO_3$, (I) 14.19, (II) 17.11.
Calc. for $C_{14}H_7O_2NI_2$: I, 53.44. Found: (I) 53.86, (II) 53.74.

Dimorphism.

4,5-Diiodophthalanil is soluble in about 8 parts of boiling xylene or 50 of boiling acetic acid. It crystallized from these solvents in pale yellow needles which melt as stated above, if the usual method of powdering the substance and heating it slowly is employed. If the unpowdered crystals, however, are heated fairly rapidly they melt about 10° lower, *i. e.*, at 231.5–233.0° (corr.). This is then the true melting point of the needles, that is, of the modification stable at temperatures below the boiling point of xylene. This form is not stable at its melting point, but especially when powdered changes slowly to the modification melting at 241.5–243° (corr.). This modification is not obtained, as might be expected, when a sample of the other form is melted and allowed to cool fairly rapidly. The formation of the needle modification under these conditions is due to the greater tendency toward supersaturation of the other form. By very slow cooling the melted anil was crystallized in pale yellow hexagonal plates. These showed no tendency to melt or change at 231°, but melted at the higher temperature. Attempts by the use of seeding to crystallize the anil from xylene and ethyl acetate in the form showing the higher melting point were unsuccessful. Only needles were obtained.

It is evident that 4,5-diiodophthalanil has a transition point somewhere between room temperature and 231°.

3,4,6-Triiodophthalic Anhydride.—The benzene extract[1] containing triiodophthalic anhydride was treated with acetic anhydride and concentrated. The product was recrystallized several times from benzene and acetic acid yielding bright yellow rhombic pyramids melting at 230–231° (corr.).

Subst. (I) 0.3442, (II) 0.4569; cc. 0.1 *N* $AgNO_3$, (I) 19.65, (II) 26.00.
Calc. for $C_8HO_3I_3$: I, 72.41. Found: (I) 72.46, (II) 72.22.

[1] Page 222.

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3,4,6-Triiodophthalic anhydride is dissolved by about 5 parts of boiling benzene or 20 parts of boiling acetic acid. When it is dissolved in sodium hydroxide solution and precipitated carefully with an excess of hydrochloric acid minute needles are formed which are probably the triiodo-acid, but efforts to isolate this substance were unsuccessful due to the ease with which it loses water even in aqueous suspension. The mono-sodium salt is only slightly soluble in water but not quite so readily precipitated as that of 4,5-diiodophthalic acid.

Hydrolysis of 3,4,6-Triiodophthalic Acid.—Forty grams of 3,4,6-triiodophthalic anhydride with 80 g. of sodium hydroxide were dissolved in 700 cc. of water and boiled for $2^3/_4$ hours, concentrating to about 150 cc. The solution was acidified with a large excess of hydrochloric acid and extracted with ether. On concentration and cooling the extract gave about 2 g. of crystals which proved to be 3,6-dihydroxyphthalic acid. After recrystallization from acetone and then water, the product, which was partly colorless and partly a greenish brown, melted at about 216–218° (corr.), (rapid heating) giving off water and forming impure anhydride. Brunner[1] records a melting point of 219–220° and mentions the two colors. The colors given by ferric chloride with an aqueous solution of the acid agree with those observed by Brunner, *i. e.*, a blue-violet changing nearly to black with excess, but when dilute solutions are used excess of ferric chloride gives an amber color.

More of the 3,6-dihydroxyphthalic anhydride was obtained by adding concentrated hydrochloric acid and xylene to the concentrated ether extract mentioned above. The mixture was then boiled until all of the aqueous hydrochloric acid had distilled off. The hot xylene was filtered off and the process repeated with the residue until 1500 cc. of xylene solution were obtained which was then boiled with boneblack and concentrated to 200 cc., yielding 3 g. of crude 3,6-dihydroxyphthalic anhydride on cooling. This was purified by two recrystallizations from anhydrous ether, melting then at 234.5–236.5° (corr.) with very slight evolution of gas. Brunner gives 232–233°.

As an additional test of its identity a sample of the anhydride was warmed an hour with acetic anhydride. A large excess of hot ligroin was added which caused the diacetate to separate on cooling in colorless leaflets. Two recrystallizations from ligroin deposited each time small compact colorless prisms that apparently represented a polymorphic modification more stable at room temperature than the leaflets. The melting points of the crystals from each of the three crystallizations were practically the same, that of the final product being carefully determined as 155.5–156.5° (corr.). Brunner gives 156–156.5° (corr.).

In addition to 3,6-dihydroxyphthalic acid small amounts of other sub-

[1] *Monatshef. Chem.*, **34**, 924 (1913).

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stances were found among the hydrolysis products of the triiodophthalic acid. Crystals of a substance containing halogen were obtained by concentrating the xylene mother liquor from which the dihydroxy anhydride had separated. A substance almost insoluble in xylene but soluble in ether was also found. It contained no halogen, gave no precipitate with lead acetate, practically no color with ferric chloride, gave the anthrachrysone test, and showed a melting point of about 230–235° (corr.). These properties agree with those recorded for 3,5-dihydroxybenzoic acid[1].

3,4,6-Triiodophthalanil.—Eighty grams of 3,4,6-triiodophthalic anhydride dissolved in two liters of boiling acetic acid were treated with 40 g. of aniline. The mixture was boiled about a minute longer and then allowed to cool. A yield of 82 grams, 89% of the theoretical, was obtained. This was recrystallized three times from xylene using boneblack. The product then had a melting point of 254.5–255.5° (corr.), unchanged by a recrystallization. The anil is soluble in about 18 parts of boiling xylene from which it crystallizes in light yellow microscopic needles.

Subst. (I) 0.3524, (II) 0.3161; cc. 0.1 *N* $AgNO_3$, (I) 17.56, (II) 15.74.
Calc. for $C_{14}H_6O_2NI_3$: I, 63.37. Found: (I) 63.24, (II) 63.20.

3,4-Dichloro-5,6-diiodophthalic Anhydride.—Fifty-four grams of 3,4-dichlorophthalic anhydride and sixty-four grams of iodine were dissolved in 250 g. of 50% fuming sulfuric acid and heated for 20 hours at 100°, 4 hours at 150°, and ½-hour at 200°. The mixture was transferred to a porcelain dish and treated when cold with 500 cc. of water. Sodium sulfite was added to remove free iodine and the yellow crystalline anhydride then filtered off. The product was freed from sulfuric acid by digestion with water at 100°. The yield was 106 g., 90% of the theoretical. This was recrystallized twice from acetic acid using boneblack, after which recrystallization did not change its melting point of 229.5–230.5° (corr.). One gram of the anhydride dissolves in 9 cc. of acetic acid, from which it crystallizes in yellow prisms. The substance was analyzed for iodine and chlorine by heating with lime, titrating the soluble halides formed, and weighing the resulting silver halides.

Subst. (I) 0.4101, (II) 0.2331; cc. 0.1 *N* $AgNO_3$, (I) 34.59, (II) 19.79; weight of AgCl + AgI, (I) c.6538, (II) 0.3766.

Calc. for $C_8O_2Cl_2I_2$: Cl, 15.13; I, 54.15. Found: Cl, (I) 14.98; (II) 14.65; I, (I) 53.47, (II) 55.31.

3,4-Dichloro-5,6-diiodophthalanil.—The anhydride dissolved in boiling acetic acid was treated with its own weight of aniline. After two minutes boiling the mixture was allowed to cool and then filtered. On recrystallization from xylene light yellow needles were obtained having a melting point of 242.5–243.5° (corr.), unchanged by recrystallization. One gram dissolves in about 9 cc. of boiling xylene.

[1] Beilstein, 1746.

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Subst. (I) 0.4177, (II) 0.2475; cc. 0.1 *N* $AgNO_3$, (I) 30.85, (II) 18.33; weight of AgCl + AgI (I) 0.5774, (II) 0.3431.

Calc. for $C_{14}H_8O_2NCl_2I_2$: Cl, 13.04, I, 46.67. Found: Cl, (I) 13.65, (II) 13.68, I, (I) 44.92, (II) 45.08.

3,6-Dichloro-4,5-diiodophthalic Anhydride.—A solution of 217 g. of 3,6-dichlorophthalic anhydride and 254 g. of iodine in 1 kg. of 50% fuming sulfuric acid was heated to 100° for 20 hours. The temperature was gradually raised to 170° during the next 6 hours. At this point the mixture was poured out and allowed to cool. The crude anhydride was separated as described for the product from 3,4-dichloro anhydride. It weighed 453 g., representing a 97% yield, but was found to contain a considerable amount of tetraiodophthalic anhydride. This impurity was easily removed by extracting with boiling benzene, after conversion of the main product into the acid, and identified by a mixed melting point. This conversion was effected by digesting the mixture with water at 95° for about 10 hours. The tetraiodophthalic anhydride was not affected by this treatment but the 3,6-dichloro-4,5-diiodophthalic anhydride was slowly acted on by the hot water, giving colorless leaflets of the corresponding acid. After complete extraction with boiling benzene, the residue was reconverted into anhydride by recrystallization from acetic acid containing an excess of acetic anhydride. It formed yellow prisms melting at 258–258.5° (corr.).

Subst. (I) 0.2265, (II) 0.2705, cc. 0.1 *N* $AgNO_3$, (I) 19.45, (II) 23.17; weight of AgCl + AgI, (I) 0.3646, (II) 0.4357.

Calc. for $C_8O_3Cl_2I_2$: Cl, 15.13; I, 54.15. Found: Cl, (I) 15.77, (II) 15.52; I, (I) 52.57, (II) 53.25.

One gram of 3,6-dichloro-4,5-diiodophthalic anhydride dissolves in 20 cc. of boiling acetic acid, readily taking up water if any is present in the solvent. One gram dissolves in 3 cc. of boiling xylene from which it crystallizes in nearly colorless needles containing xylene of crystallization shown by their efflorescence when exposed to air.

3,6-Dichloro-4,5-diiodophthalanil.—This was prepared as described for 3,4-dichloro-4,5-diiodophthalanil. Light yellow needles were obtained melting at 232–232.5° (corr.).

Subst. (I) 0.2842, (II) 0.4332; cc. 0.1 *N* $AgNO_3$, (I) 20.95, (II) 31.90; weight of AgCl + AgI, (I) 0.3945, (II) 0.5995.

Calc. for $C_{14}H_8O_2NCl_2I_2$: Cl, 13.04; I, 46.67. Found: Cl, (I) 13.29, (II) 13.38; I, (I) 46.00 (II) 45.55.

One gram of the anil dissolves in 6 cc. of boiling xylene or 40 cc. of boiling acetic acid.

The attempt was made to replace halogen in the anil by boiling in aniline for 2 hours. Only tarry products were obtained except a small amount of impure substance, evidently unchanged anil, melting at 211–217° (corr.).

4,5-Dichloro-3,6-diiodophthalic Anhydride. — The details of this

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preparation were the same as given for the iodination of 3,4-dichlorophthalic anhydride. The yield was 110 g., 93% theoretical. After three recrystallizations from acetic acid using boneblack, the product melted at 232.5–233.5° (corr.). One gram dissolves in 8 cc. of boiling acetic acid, separating on cooling in the form of large jagged yellow blades.

Subst. (I) 0.3063, (II) 0.2372; cc. 0.1 *N* $AgNO_3$, (I) 25.80, (II) 20.13; weight of AgCl + AgI, (I) 0.4863, (II) 0.3841.

Calc. for $C_8O_3Cl_2I_2$: Cl, 15.13; I, 54.15. Found: Cl, (I) 15.13, (II) 14.48; I, (I) 52.78, (II) 55.93.

4,5-Dichloro-3,6-diiodophthalanil.—This substance was made like its above mentioned isomers, and after two recrystallizations from xylene and one from acetic acid melted at 282.5–284° (corr.). One gram of the anil dissolves in 18 cc. of boiling xylene or 140 cc. of boiling acetic acid. It crystallizes from these solvents in very pale yellow needles.

Subst. (I) 0.2573, (II) 0.1615; cc. 0.1 *N* $AgNO_3$, (I) 18.79, (II) 12.03; weight of AgCl + AgI, (I) 0.3529, (II) 0.2250.

Calc. for $C_{14}H_5O_2NCl_2I_2$: Cl, 13.04, I, 46.67. Found: Cl, (I) 13.30, (II) 13.80; I, (I) 45.09, (II) 45.20.

3,6-Dianilino-4,5-dichlorophthalanil.—Twenty grams of 4,5-dichloro-3,6-diiodophthalanil were heated with 100 g. of aniline for 24 hours at 130°. The temperature was then kept at about 175° for four hours. A very small yield of orange-red crystals was obtained by the treatment described in the case of the isomeric product from tetrachlorophthalanil[1].

The product melted at 181.5–185° (corr.). Its isomer obtained from tetrachlorophthalanil melted at 182.5–183.5° (corr.), and a mixture of the two at about 156–173° (corr.). These melting points show that the sample was impure but entirely distinct from the previously obtained product. Unfortunately the amount in hand was insufficient for further purification, but qualitative tests showed that the substance contained no iodine, and a lime combustion showed that it had approximately the composition of a dianilino dichlorophthalanil:

Subst. (I) 0.1088; cc. 0.1 *N* $AgNO_3$, 5.39.

Calc. for $C_{26}H_{17}O_2N_3Cl_2$: Cl, 14.96. Found: 17.57.

Summary.

(I) The partial iodination of phthalic anhydride has been effected, an easy method of separating the four products worked out, and their structures established.

(II) The iodination of three dichlorophthalic acids has been effected.

(III) Silver salts in pyridine solution have been found to act readily on certain iodinated phthalic acids, forming 3-hydroxy-6-iodophthalic acid from the corresponding diiodo derivative.

(IV) Sodium hydroxide solutions hydrolyze the iodinated phthalic acids, often yielding at the same time both oxidation and reduction prod-

[1] THIS JOURNAL, 40, 198 (1918).

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ucts. In this way a number of hydroxyl derivatives have been prepared by new methods, in particular 3-hydroxyphthalic acid. The anhydride of this substance has been obtained in much purer condition than samples previously recorded, and several of its derivatives prepared.

(V) The anils of the new iodinated phthalic acids have been prepared and one of them found to exhibit dimorphism.

(VI) Iodine in the nucleus of phthalic acid does not react smoothly with aniline, but a small yield of 3,6-dianilino-4,5-dichlorophthalanil has been obtained from the corresponding iodinated derivative.

(VII) A spectroscopic study of the new iodinated phthalic acids will be reported in a later paper.

PITTSBURGH, PA.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF PITTSBURGH.]

PHTHALIC ACID DERIVATIVES CONSTITUTION AND COLOR. VIII.[1] TETRAIODOFLUORESCEIN AND SOME OF ITS DERIVATIVES.

BY DAVID S. PRATT AND ARTHUR B. COLEMAN.

Received October 17, 1917.

A large and important class of dyes resulting from introducing chlorine into the phthalic acid residue of fluorescein with or without halogens in the resorcin portions of the molecule is recognized at the present time. Among these might be mentioned eosin, erythrosin, phloxine and a variety of their chorine derivatives. Some are especially valuable as stains and indica tors, others for dyeing silks delicate shades of red and pink.

Tetraiodofluorescein, or fluorescein with four atoms of iodine substituted in the phthalic anhydride molecule, had never been prepared. The substitution of iodine in such a colored substance, especially iodine in large amount, might be expected to show some interesting results. As is well known the effect of substituting halogen for hydrogen in many compounds especially dyes, is frequently to increase the period of molecular vibration, or, in other words, to shift the absorption of light toward the longer wave lengths. This modifies the shade of color and might result in producing desirable new dyestuffs.

Iodine is an unsaturated atom possessing considerable residual affinity and chemical activity in excess of that shown by other halogens. This activity should result in various proximity effects modifying the tendency to produce a lactone ring and altering the equilibrium between benzenoid and quinoid condition depending upon this ring. It was also with the view of obtaining information relating color and chemical constitution that we undertook the study of these derivatives.

Fluorescein itself and its related compounds exist in either of two isomeric

[1] THIS JOURNAL, 40, 198 (1918).

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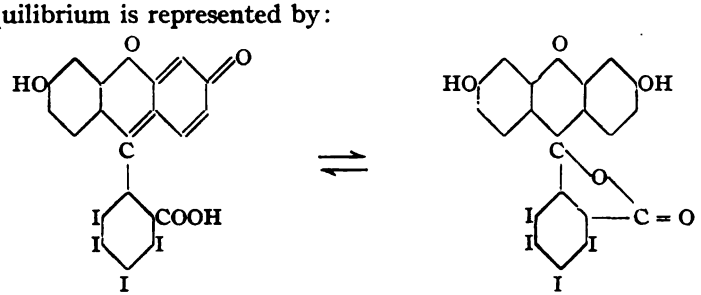
forms, the benzonoid without marked color or the quinoid with vivid color and more or less fluorescence. Fluorescein is known only in the colored condition and undoubtedly is correctly portrayed by the latter structure regardless of the question of intra-molecular interaction between quinoid and benzenoid rings which probably is responsible for its intense color.

It has already been shown that four chlorine atoms in the phthalic acid part of the molecule alter this equilibrium.[1] It was expected that iodine substitution would show even more important effects. An indication of this is evident when colorless phthalic or tetrachlorophthalic anhydride is compared with yellow tetraiodophthalic anhydride. The effect is also evident when one remembers that phthalic acid loses water with some difficulty to form its anhydride whereas tetraiodophthalic acid requires only brief heating to accomplish the same conversion. We have carried this substitution up to eight atoms in making the octaiodofluorescein.

It was also our intention to study the absorption spectra of the entire series with the most improved absorption apparatus, but war conditions made it impossible for Adam Hilger, London, to construct the necessary equipment. This portion of the work will be reported at a later date.

Tetraiodofluorescein was prepared from tetraiodophthalic anhydride[2] in a number of ways. It dissolves in alkaline solutions with a yellowish red color and vivid green fluorescence closely resembling that given by the parent substance. Acidification causes the precipitation of a golden yellow hydrate, soluble in various organic solvents and fairly stable at room temperature. The hydrate loses water when heated and at the same time changes from golden yellow to reddish brown.

Tetraiodofluorescein is entirely different from ordinary fluorescein in that it lies on the border line of equilibrium between the benzenoid and the quinoid form, with the latter probably metastable at ordinary temperatures. This equilibrium is represented by:



Quinoid. Benzenoid.

Ready means of passing either way have been found. It is quite probable that the hydrate is a derivative of the second structure but it shows certain reactions which differentiate it from other similar hydrates described in the

[1] Orndorff and Hitch, THIS JOURNAL, 36, 680 (1914).

[2] See Pratt and Shupp, *Ibid.*, 40, 254 (1918).

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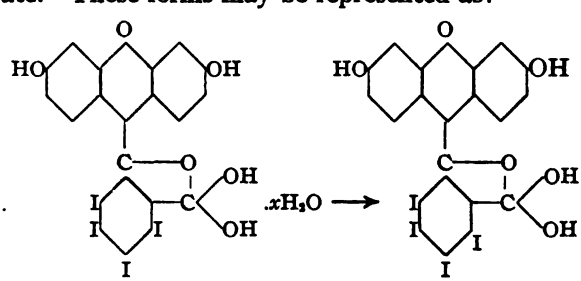
literature. When freshly precipitated by acidification of a dilute solution in alkali, the hydrate undoubtedly contains water attached to the molecule in two distinct ways. An unknown per cent. of water of constitution is lost rapidly at room temperature as the moist hydrate dries. It was not found possible to obtain analytical data on this point since the hydrate is amorphous and dries slowly. During this loss of water the color remains unchanged. The product attained constant weight within a few days and still possessed a golden yellow color. When it was heated at 120° in an oven it slowly lost weight corresponding approximately to one molecule of water, and the color darkened somewhat to a reddish brown.

We shall speak of the original hydrate as hydrous tetraiodofluorescein hydrate, the air-dried product as hydrous tetraiodofluorescein, and the final material as anhydrous tetraiodofluorescein. The three forms show distinct reactions serving to differentiate them sharply from each other. The loss of water at room temperature takes place so readily that it probably represents loss of water held loosely by molecular combination. Partial loss of this water can be brought about by boiling the hydrate suspended in water. The water still held by the hydrous tetraiodofluorescein is retained more firmly, so much so in fact that it is driven off with difficulty even at 120°. This molecule is best represented as water of constitution, and its presence in the compound explained by the action of the four negative iodine atoms in much the same way as in chloral hydrate. These forms may be represented as:



Hydrous tetraiodofluorescein hydrate (yellow). Hydrous tetraiodofluorescein (yellow).

Heating hydrous tetraiodofluorescein at 120° for sufficient time to drive off its molecule of water *partially* converts the benzenoid form into the quinoid as is shown by the increase in color. It should be remembered that ordinary fluorescein is deep red and has never been isolated in the colorless benzenoid condition except in the form of certain derivatives such as acetate, benzoate, etc. The conversion to *quinoid* form is only partial in the case of the tetraiodofluorescein and even this change represents the formation of a metastable condition.

A drop of acetone, alcohol, or ethyl acetate applied to the reddish brown anhydrous tetraiodofluorescein causes an immediate change to clear canary-

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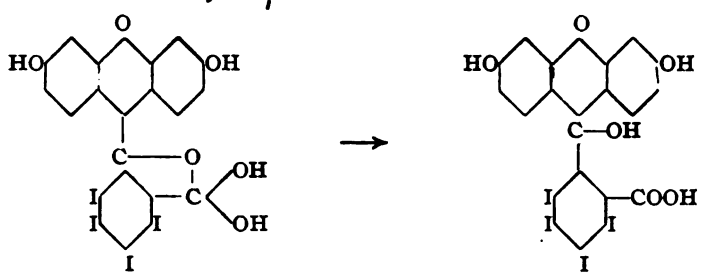
yellow, probably because some of the compound dissolves and in solution readily rearranges to the stable form. There is also a loose molecular addition product formed between tetraiodofluorescein and solvent, especially in the case of ethyl acetate, but the solvent of crystallization is readily driven off by gentle warming. This gives an excellent means of obtaining benzenoid tetraiodofluorescein free from the colored quinoid isomer. The benzenoid form is yellow instead of colorless simply because the parent tetraiodophthalic anhydride is this color.

When hydrous tetraiodofluorescein is treated with a little methyl or ethyl alcohol it immediately turns nearly colorless forming the carbinol carboxylic acid. This results easily from a slight rearrangement of the molecule as indicated by the structures



Hydrous tetraiodofluorescein (golden yellow). Tetraiodofluorescein carbinol carboxylic acid (nearly colorless).

The carbinol carboxylic acid may be obtained in the form of faintly yellow, well-formed crystals by slow evaporation of a methyl alcohol solution. It differs in this respect from both the isomeric hydrous tetraiodofluorescein and tetraiodofluorescein, neither of which have ever been obtained crystalline.

The carbinol acid loses a molecule of water on heating at 100° and gives the yellow benzenoid tetraiodofluorescein. Further heating at 180° for only five minutes carries the equilibrium toward the quinoid form with its reddish brown color but without change in weight. The carbinol acid gives the same diacetate with acetic anhydride as the hydrous or anhydrous compound.

Anhydrous tetraiodofluorescein gives a reddish orange monopotassium salt when an alcoholic solution is heated with alcoholic potassium acetate. The salt crystallizes rather well from alcohol and is difficultly soluble in water, giving, however, a fluorescent solution. The red-orange color changes to deep red when caustic alkali is added, and the more readily soluble dipotassium salt is formed. The structure of the monopotassium salt is doubtless the usual quinoid one.

Dry ammonia gas acts on anhydrous tetraiodofluorescein rapidly giving a deep red diammonium salt, difficultly soluble in cold water, readily on heating. It is quite stable when exposed to the air, but loses all its am-

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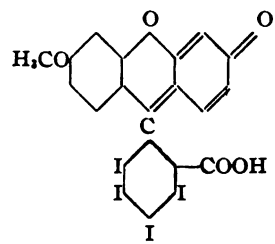
monia on heating at 100°, giving again the red anhydrous tetraiodofluorescein.

The monosilver salt was obtained in the form of an amorphous violet-red powder. It was hoped that this silver salt, which undoubtedly also has the structure assigned to the monopotassium salt, would react with alkyl iodides to give corresponding quinoid esters, but this could not be accomplished. Some reaction took place but no pure ester could be isolated.

The monomethyl ether of tetraiodofluorescein shows a very brilliant red color indicating a quinoid structure represented by



The ether is very slightly soluble with fluorescence in dilute sodium hydroxide, more so in concentrated solution. Its brilliant color is rather remarkable.

Tetraiodofluorescein diacetate is easily made and obtained from acetone as yellow crystals. So few of the derivatives are crystalline that the acetate offers the best means for purifying tetraiodofluorescein. The clear yellow color shows its structure to be benzenoid. The dibenzoate represents an analogous derivative, also giving pale yellow crystals.

Experimental.

Tetraiodofluorescein.—652 g. (1 mol) of tetraiodophthalic anhydride were intimately mixed with 216 g. (2.1 mols) of colorless resorcin. 216 g. of finely powdered freshly fused zinc chloride were then added, the mixture placed in a roomy casserole and heated in an oil bath to 200°. The material was frequently stirred until after about two hours it became too pasty. The temperature was maintained about four hours at 200–210°, during which time the color darkened to almost black.

The melt was finely powdered and extracted with boiling dilute hydrochloric acid until free from zinc salts. This changed the color to canary-yellow. The tetraiodofluorescein was then dissolved out with successive small portions of five per cent. sodium hydroxide, the solution diluted to three liters and precipitated by adding three per cent. hydrochloric acid while thoroughly stirring with a blast of air. The hydrate separated in a yellow amorphous form which was washed by decantation, filtered and dried at 120°. Yield of impure product, 95% theoretical.

Phosphorus pentoxide was tried as a condensing agent, but the reaction was too vigorous, the temperature rose to about 230° and the yield was

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very small. Some condensing agent, however, must be used as a trial fusion of anhydride and resorcin alone gave only a five per cent. yield, the greater part of the former remaining unchanged.

The purification of tetraiodofluorescein presented many difficulties. 100 g. of crude material obtained as above were finely ground and extracted with two liters of anhydrous ether leaving 26 g. of gray insoluble material. The tetraiodofluorescein was removed from the ether by shaking with five per cent. sodium hydroxide solution until no color was imparted to the alkali. The addition of dilute acid to this extract gave a copious precipitate of light pink hydrate which was washed free from chlorides, and dried to constant weight at 120°. Yield, 73 g. The method is tedious and the resulting product not quite pure as shown by analysis:

Subst. 0.3019; cc. 0.1 *N* $AgNO_3$, 12.90.
Calc. for $C_{20}H_8O_5I_4$: I, 60.49. Found: 54.23.

This analysis is given as representing the degree of purity which may be expected from this method of purification.

The second method used was based upon obtaining pure diacetate which was then saponified to pure fluorescein. 100 g. of crude material as above were finely powdered and suspended in 300 cc. of acetic anhydride in a roomy flask. 10 g. of freshly fused sodium acetate were added, and the mixture heated 30 minutes in a water bath. The temperature was then raised sufficiently to cause gentle boiling, and maintained for one hour, at the same time taking care that no material adhered to the flask and thereby became charred.

The reaction is complete when all the dark-colored tetraiodofluorescein has changed to the yellow diacetate. The mixture was poured after cooling into hot water, and the acetate carefully washed, dried at 110°, then ground to a fine powder and rewashed with hot water. It was dried again and dissolved in acetone giving a dark red-colored solution. This was boiled with successive portions of boneblack for a period of five days when the color became amber-yellow. Concentration to one-fourth its volume and cooling gave the acetate in yellow crystals. These were recrystallized several times from acetone until pure as shown by analysis. The lime combustion method was used.

Subst. (I) 0.2847, (II) 0.4232; cc. 0.1 *N* $AgNO_3$, (I) 12.40, (II) 18.42.
Calc. for $C_{24}H_{12}O_7I_4$: I, 55.20. Found: (I) 55.28, (II) 55.23.

The crystalline diacetate is attacked very slowly by aqueous alkali but alcoholic alkali cannot be used as it removes iodine. The acetate is best saponified by first dissolving it in acetone and pouring this solution into a dilute alkaline solution. The result is a flocculent, amorphous form of the acetate which is much more readily attacked. 100 g. of pure diacetate were added in this way to a liter of 5% aqueous sodium hydroxide solution and the suspension stirred mechanically until complete solution was

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effected. Acidification of the red highly fluorescent alkaline solution caused the hydrated tetraiodofluorescein to precipitate as a canary-yellow jelly. This was washed six times by decantation using large amounts of water, vigorous stirring, followed by settling. The material was then filtered, washed with hot water until free from chlorides, and dried to constant weight of 120°. This gave anhydrous fluorescein.

Subst. (I) 0.3910, (II) 0.2570; cc. 0.1 *N* $AgNO_3$, (I) 18.78, (II) 12.21.
Calc. for $C_{20}H_8O_5I_4$: I, 60.49. Found: (I) 60.96, (II) 60.29.

The yield was about 50% pure product calculated on the basis of crude material. The red anhydride treated with acetone, ether, or alcohol changes at once into a canary-yellow form.

Hydrous Tetraiodofluorescein.—The canary-yellow material obtained as above was air-dried instead of at 120° without marked darkening in color. It reached constant weight after 30 days whereupon it was heated at 110°. The loss in weight corresponded approximately to one molecule of water and the color changed to the reddish brown of anhydrous tetraiodofluorescein.

Subst. 3.8512 g. loss 0.0526 g.
Calc. for $C_{20}H_8O_5I_4.H_2O$: H_2O, 2.11. Found: 1.36.

Hydrous tetraiodofluorescein is readily soluble in ether giving a yellow solution which deposits a light yellow product on evaporation. A drop of ether applied to the hydrate does not appreciably change its color as it does in the case of the anhydrous material. It gives no color in the cold with dimethylaniline.

Tetraiodofluorescein Carbinol Carboxylic Acid.—Hydrous tetraiodofluorescein was treated with methyl alcohol which caused the color to change at once to a very pale yellow. The resulting carboxylic acid was dissolved in methyl alcohol and obtained upon concentrating as a light yellow, amorphous substance. Very slow concentration by evaporation gave pale yellow, well-formed crystals of the same compound.

An air-dried sample lost weight on heating at 100° corresponding approximately to one molecule of water.

Subst. (I) 0.6212, loss 0.0231 g. at 100°.
Calc. for $C_{20}H_{10}O_6I_4$: H_2O, 2.06. Found: 3.71.

During drying the color deepened to that of benzenoid tetraiodofluorescein. Further heating for five minutes at 170-180° caused the appearance of the reddish brown color characteristic of the quinoid product but with no change in weight. The heating at 170° was continued for 4 hours but there was no loss of weight.

Diammonium Salt.—Dry ammonia gas passed over weighed amounts of anhydrous tetraiodofluorescein gave this salt. Constant weight was reached within 12 hours.

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Subst. 0.3995 g., gain in weight 0.0176 g.
Calc. for $C_{20}H_8O_5I_4.2NH_3$: NH_3, 3.91. Found: 4.21.

The red diammonium salt loses its ammonia easily at 100° giving the original reddish brown tetraiodofluorescein.

Subst. 0.7434 g., loss in weight 0.0286 g.
Calc. for $C_{20}H_8O_5I_4.2NH_3$: NH_3, 3.91. Found: 3.84.

Tetraiodofluorescein Dibenzoate.—The dibenzoate was prepared both by the Baumann-Schotten reaction and by boiling anhydrous tetraiodofluorescein in benzoyl chloride. The resulting product was the dibenzoate in each case although it was thought probable that the former method would give a monobenzoate.

10 g. of tetraiodofluorescein were dissolved in 200 cc. of 5% sodium hydroxide solution and treated with successive portions of benzoyl chloride until the red color disappeared. The crude benzoate was washed with dilute warm alkaline solution, followed by warm water, and crystallized several times from chloroform in the form of pale yellow crystals. The yield of crude dibenzoate is nearly theoretical, that of pure product about 30%.

In the second method of preparation 10 g. of tetraiodofluorescein were suspended in 75 cc. of benzoyl chloride. This was gently boiled for 30 minutes and poured into alcohol which separated the benzoate as a grayish green amorphous mass. This was filtered off, washed with hot water and dried. The solution in chloroform was boiled with boneblack until almost colorless and the benzoate finally recrystallized from acetone. It melted at 288° (corr.) and showed no depression of the melting point when mixed with the previous product. They are identical.

Subst. (I) 0.2362, (II) 0.2282; cc. 0.1 *N* $AgNO_3$, (I) 9.03, (II) 8.80.
Calc. for $C_{34}H_{16}O_7I_4$: I, 48.63. Found: (I) 48.52, (II) 48.94.

Monopotassium Salt.—In the preparation of this salt 5 g. of tetraiodofluorescein were dissolved in 150 cc. of absolute ethyl alcohol, giving an amber-colored solution. To this was added an alcoholic solution containing 2 g. of anhydrous potassium acetate, both solutions being hot when mixed. The color changed at once to red and the salt began to deposit in shining, red crystals. It was recrystallized from alcohol in which it is very sparingly soluble. Yield, about 50 %.

Subst. (I) 0.2137; cc. 0.1 *N* $AgNO_3$, 9.84.
Calc. for $C_{20}H_7O_5I_4K$: I, 58.16. Found: 58.44.

The dipotassium salt is much more soluble in water and difficult to purify.

Tetraiodofluorescein Monomethyl Ether.—Dimethyl sulfate was added in small portions with vigorous shaking to a weakly alkaline solution of tetraiodofluorescein. Dilute alkali was added from time to time to replace that used up by the dimethyl sulfate and to keep the solution from becoming acid. It was found to be advantageous to shake vigorously

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as this gave a more finely divided product easier to purify. The solution became less and less red, and its green fluorescence almost entirely disappeared. The resulting ether separated as an insoluble, amorphous, fiery red mass which was filtered off, washed, dried and finely powdered. It was extracted with two per cent. sodium hydroxide solution until the filtrate gave no precipitate on acidifying, and finally washed with water and dried.

The bright red powder was quite soluble in ethyl alcohol, more so in methyl alcohol and acetone, but all attempts to crystallize it failed. Purification was finally accomplished by repeatedly dissolving in methyl alcohol and partially separating by concentrating the solvent. The ether was finally treated with strong potassium hydroxide solution to saponify any methyl ester present and repurified from methyl alcohol. This procedure gave a brick red product slightly soluble with fluorescence in strong alkali. It decomposed on heating at about 251°.

Subst. (I) 0.3491, (II) 0.1700; cc. 0.1 *N* $AgNO_3$, (I) 16.26, (II) 8.05.
Calc. for $C_{21}H_{10}O_5I_4$: I, 59.74. Found: (I) 59.15, (II) 60.10.

Methoxyl was determined by the Zeissel method.

Subst. (I) 0.3254, (II) 0.2327; g. AgI, (I) 0.0945, (II) 0.0740.
Calc. for $C_{21}H_{10}O_5I_4$: CH_3O, 3.65. Found: (I) 3.84, (II) 4.20.

Silver Salt.—5 g. of pure tetraiodofluorescein were dissolved in 10 cc. of concentrated ammonium hydroxide and the solution diluted to 400 cc. A 10% silver nitrate solution containing a slight excess of silver was then added. The color changed at once to a deeper red but no precipitation occurred until the excess of ammonia was boiled off. The silver salt gradually deposited during the boiling as a violet-red powder which was filtered off, washed with water, finally boiled with water for 30 minutes, and washed until the filtrate gave only a slight test for silver. It was not possible to remove all adsorbed silver as the salt could not be obtained crystalline. The product dried at 120° was analyzed as follows:

A weighed sample was suspended in 25 cc. of six normal nitric acid and allowed to stand about 12 hours at room temperature. The solution was diluted to 400 cc., filtered, and the silver nitrate titrated with standard ammonium thiocyanate using ferric alum as indicator.

Subst. (I) 0.1431, (II) 0.3918; cc. 0.1 *N* NH_4SCN, (I) 1.21, (II) 4.23.
Calc. for $C_{20}H_7O_5I_4Ag$: Ag, 11.44. Found: (I) 11.48, (II) 11.65.

Summary.

1. Tetraiodofluorescein has been prepared. It exists at ordinary temperatures as an unstable mixture of benzenoid and quinoid modifications.

2. The yellow hydrate loses a part of its water readily to give a yellow hydrous derivative. This then loses a molecule of water on heating to give anhydrous tetraiodofluorescein.

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3. Alcohol acting on the hydrate converts it into the pale yellow carbinol-carboxylic acid.

4. Acetone on the anhydrous material gives a lemon yellow acetonate which loses acetone to give benzenoid tetraiodofluorescein.

5. Benzenoid tetraiodofluorescein rapidly rearranges into the red quinoid form at 180°.

6. The monopotassium salt was prepared in reddish orange crystals.

7. Dry ammonia on tetraiodofluorescein gives a deep red salt with gain in weight corresponding to a diammonium salt.

8. The red silver salt and monomethyl ether are characteristic of the quinoid form, while the yellow diacetate and dibenzoate, the yellow tetraiodofluorescein and carbinol acid characterize the benzenoid type.

9. Absorption spectra of the entire series will be reported in a later paper.

PITTSBURGH, PA.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF PITTSBURGH.]

PHTHALIC ACID DERIVATIVES; CONSTITUTION AND COLOR, IX.[1] TETRAIODOEOSIN AND SOME OF ITS DERIVATIVES.

BY DAVID S. PRATT AND ARTHUR B. COLEMAN.

Received October 17, 1917.

Tetraiodofluorescein[2] in the anhydrous condition readily takes up four atoms of bromine, replacing hydrogen in the two resorcin residues. For this purpose 10 g. were suspended in 500 cc. of glacial acetic acid containing 10 cc. of bromine and the mixture boiled gently for an hour. The reddish brown tetraiodofluorescein gradually changed to a yellow crystalline substance. After cooling this was filtered off and washed with 40% alcohol until the filtrate gave no test for halogen. The product was heated to constant weight at 105° and found to be pure tetraiodoeosin. Yield, theoretical.

The material was analyzed by the lime combustion method, filtering off all acid-insoluble material before adding silver nitrate. Titration values and weight of combined silver halides gave the necessary data:

Subst. (I) 0.3946, (II) 0.4656; cc. 0.1 *N* $AgNO_3$, (I) 26.86, (II) 29.10. Weight AgI + AgBr, (I) 0.5674, (II) 0.6468.

Calc. for $C_{20}H_4O_5Br_4I_4$: Br, 27.76; I, 44.09. Found: (I) Br, 27.19, I, 43.19, (II) Br, 27.63; I, 43.88.

Tetraiodoeosin forms canary-yellow crystals which show no tendency whatever to go over into the highly colored quinoid form. It should be represented, therefore, by the structure

[1] THIS JOURNAL, 40, 198 (1918).

[2] *Ibid.*, 40, 236 (1918).

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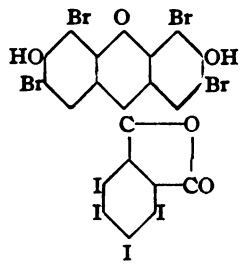

Tetraiodoeosin (yellow).

The yellow color represents the effect due to four iodine atoms in the phthalic anhydride residue, the tetraiodo anhydride itself being canary-yellow.

Tetraiodoeosin is slightly soluble in acetone, ethyl acetate and benzol, practically insoluble in alcohol. Alcohol does not cause a rearrangement into the carbinol carboxylic acid as in the case of tetraiodofluorescein. It decomposes upon heating to about 200° with loss of iodine, and is very sensitive to alkalies, giving a deep red solution with faint greenish fluorescence. It should therefore be valuable as an indicator.

Tetraiodoeosin Hydrate.—A dilute alkaline solution of tetraiodoeosin was acidified by adding a slight excess of 2 % hydrochloric acid, giving an abundant precipitation of pink amorphous hydrate which was allowed to settle. It was washed as free from chlorides as possible, filtered, and air-dried to constant weight. Attempts to crystallize it always gave yellow anhydrous tetraiodoeosin.

The air-dried hydrate lost weight on heating at 140° as follows:

Subst. 7.2552 g., loss in weight, 0.0372 g.
Calc. for $C_{20}H_4O_5Br_4I_4.H_2O$: H_2O, 1.54. Found: 0.51.

This would indicate one-third of a molecule of water, but the hydrate is so unstable it probably lost water during air-drying. In fact it was noticed that boiling a suspension of hydrate in water caused a lessening of the pink color, although it never became the clear yellow of anhydrous tetraiodoeosin.

Diammonium Salt.—A weighed sample of tetraiodoeosin was placed in a porcelain boat and subjected to the action of dry ammonia gas. The color slowly changed from yellow to brilliant red and the crystalline structure was destroyed. Constant weight was obtained after 24 hours.

Subst. 0.3948 g.. gain in weight, 0.0119 g.
Calc. for $C_{20}H_4O_5Br_4I_4.2NH_3$: NH_3, 2.87. Found: 2.92.

The diammonium salt is sparingly soluble in cold water, readily on heating, giving a deep red solution with slight greenish fluorescence.

When the dry salt is heated at 120° it loses two molecules of ammonia, giving amorphous yellow tetraiodoeosin.

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Subst. 0.4067, loss in weight, 0.0102.
Calc. for $C_{20}H_4O_5Br_4I_4.2NH_3$: NH_3, 2.87. Found: 2.52.

The brilliant red color of the diammonium salt is evidence of its quinoid structure.

Tetraiodoeosin Diacetate.—The diacetate was prepared by gently boiling for 5 hours a suspension of 10 g. pure tetraiodoeosin in 30 cc. acetic anhydride containing 10 g. freshly fused sodium acetate. Red sodium salt at first formed around the suspended particles but these gradually reacted. The crude acetate was purified by repeated crystallization from acetone, using boneblack. The acetate forms light yellow crystals which darken with evolution of iodine at 270–280°. It is quite soluble in acetone, ethyl acetate, chloroform and benzol. The best solvent, however, appears to be a mixture of equal parts of acetone and alcohol. Yield, 92%.

The formation of diacetate does not take place as readily as in the case of tetraiodofluorescein, but once formed it is quite stable. Cold dilute alkali does not produce a trace of color, but heating with 10% sodium hydroxide causes saponification.

Subst. (I) 0.2401, (II) 0.2224; cc. 0.1 *N* $AgNO_3$, (I) 15.51, (II) 14.39.
Weight of AgI + AgBr: (I) 0.3275, (II) 0.3032.
Calc. for $C_{24}H_8O_7Br_4I_4$: Br, 25.87; I, 41.09. Found: (I) Br, 25.74; I, 40.97, (II) Br, 25.71; I, 40.83.

Tetraiodoeosin Dibenzoate.—The Baumann-Schotten method was found convenient for making the benzoate. Benzoyl chloride was added with vigorous shaking to a solution of tetraiodoeosin in dilute sodium hydroxide. The crude product separated in a sticky mass that was first thoroughly washed and dried, then dissolved in hot chloroform, and alcohol slowly added until the solution became faintly turbid. Upon cooling the benzoate separated in brownish crystals. This procedure was twice repeated. Several recrystallizations from acetone finally gave pale yellow crystals of pure benzoate which softened about 261° but gave no sharp melting point, as iodine is readily split off. The dibenzoate is readily soluble in chloroform, acetone, methyl alcohol and ethyl acetate. Yield, 40%. It is interesting to note the unusually high formula weight of 1360.

Subst. (I) 0.1593, (II) 0.2295; cc. 0.1 *N* $AgNO_3$. (I) 7.06, (II) 12.61.
Weight AgI + AgBr: (I) 0.1880, (II) 0.2679.
Calc. for $C_{34}H_{12}O_7Br_4I_4$: Br, 23.51; I, 37.34. Found: (I) Br, 22.32; I, 35.45, (II) Br, 22.20; I, 35.26.

Tetraiodoeosin Monomethyl Ether.—An alkaline solution of tetraiodoeosin was vigorously shaken with successive small portions of dimethyl sulfate, taking care to maintain alkalinity at all times. The ether so formed precipitated out as a brilliant red amorphous powder that was treated with strong potassium hydroxide solution to remove unchanged tetra-

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iodoeosin and to saponify any methyl ester which migh thave been formed, washed with water, and finally purified from acetone and methyl alcohol.

The ether is fairly soluble in ethyl ether, ethyl acetate, methyl alcohol and acetone, sparingly so in chloroform. The unusually brilliant red color shows that the quinoid structure should be given this product.

Subst. (I) 0.3954; cc. 0.1 *N* $AgNO_3$, 26.39. Weight of AgI + AgBr, 0.5616.
Calc. for $C_{21}H_6O_7Br_4I_4$: Br, 27.43; I, 43.56. Found: Br, 26.86; I, 42.66.

A methoxyl determination by the Zeissel method was made to establish beyond doubt the presence of but one methoxyl radical.

Subst. (I) 0.3147, (II) 0.0880. Weight AgI, (I) 0.0786, (II) 0.0225.
Calc. for $C_{21}H_6O_5Br_4I_4$: CH_3O, 2.75. Found: (I) 3.30, (II) 3.38.

Silver Salt.—An ammoniacal solution was prepared by dissolving 5 g. of tetraiodoeosin in 10 cc. concentrated ammonium hydroxide and diluting to about 400 cc. A slight excess of 10% silver nitrate solution was added and the solution boiled until free from ammonia. The silver salt separated gradually as a bright crimson sticky precipitate very difficult to wash or handle. On drying to constant weight at 120° it changed to a beautiful red-violet color. The dry salt was boiled several hours with absolute alcohol to free it, if possible, from adsorbed silver, but this was not entirely successful.

Subst. (I) 0.2011, (II) 0.3138; cc. 0.1 *N* NH_4SCN, (I) 2.12, (II) 3.25.
Calc. for $C_{20}H_3O_5Br_4I_4Ag$: Ag, 8.57. Found: (I) 11.37, (II) 11.17.

The analyses were made by adding an excess of six normal nitric acid and letting it stand at room temperature overnight, then diluting with water and titrating the silver nitrate with standard ammonium thiocyanate solution using ferric alum as indicator.

The silver salt is insoluble in ordinary solvents, but dissolves in ammonium hydroxide, giving a deep red solution with slight greenish fluorescence.

It was noted during the above analyses that the action of dilute nitric acid on the purple-silver salt always left a brick-red precipitate. This may have contained more or less quinoid tetraiodoeosin, but the amount available was so small it was not investigated further.

Summary.

1. Tetraiodoesin has been prepared. It exists in the benzenoid modification as canary-yellow crystals.

2. The diacetate and dibenzoate are also benzenoid.

3. The hydrate is pink, losing water very readily to give the yellow tetraiodoeosin.

4. The diammonium salt is red, and the monosilver salt a red-purple. The former loses ammonia on heating, regenerating the yellow tetraiodoeosin.

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5. Tetraiodoeosin monomethyl ether has been prepared. It shows vivid red color indicating quinoid structure.

6. The absorption spectra of this series will be reported upon in a later paper.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF PITTSBURGH.]

PHTHALIC ACID DERIVATIVES; CONSTITUTION AND COLOR, X.[1] TETRAIODOERYTHROSIN (OCTOIODOFLUORESCEIN) AND SOME OF ITS DERIVATIVES.

BY DAVID S. PRATT AND ARTHUR B. COLEMAN.

Received October 17, 1917.

Tetraiodoerythrosin or octoiodofluorescein is a new dye derived from fluorescein by substituting four iodine atoms for hydrogen in the phthalic acid residue and two in each of the resorcin residues of the molecule. Somewhat similar derivatives of ordinary fluorescein but without any iodine in the phthalic residue have been made commercially by methods of electrolysis, carrying on the reaction until the desired color has been obtained. Such compounds have varying percentages of iodine and are, *per se*, mixtures. A variety of ways were tried to obtain the definite fluorescein mentioned above with eight atoms of iodine in the molecule. An alkaline solution of tetraiodofluorescein was treated with iodine in potassium iodide solution. The mixture gradually lost its brilliant fluorescence and became light red in color, but the purified dye contained considerably less iodine than the desired tetraiodoerythrosin.

Subst. 0.3993; cc. 0.1 *N* $AgNO_3$, 20.91.
Calc. for $C_{20}H_4O_5I_8$: I, 75.80. Found: 66.46.

A second more successful method was to suspend tetraiodofluorescein in glacial acetic acid containing iodine and finely powdered potassium iodate, the latter being added to remove hydriodic acid as fast as formed. The mixture was heated in a water bath for 5 hours, during which time its color changed from dark red to orange-yellow. Longer heating or a higher temperature did not improve the yield. This method gave some of the desired product but the greater part of the material appeared to contain approximately six atoms of iodine.

The most satisfactory method found consisted in suspending 20 g. of pure tetraiodofluorescein in 200 cc. of absolute alcohol and adding to this 13 g. of iodine and 0.2 g. of iodic acid. The mixture was heated with reflux condenser for 12 hours, then diluted with water and acidified. A brown material settled out which was filtered off and heated 2 hours at 100° with glacial acetic acid containing 0.5 g. of potassium iodate, as this was found to improve the yield considerably. The material was finally filtered off and washed with dilute potassium iodide solution to remove

[1] THIS JOURNAL, 40, 198 (1918).

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free iodine, and the residue boiled with water repeatedly until the filtrate gave no test for halogen. This left a pink product which was still contaminated with lower iodinated products.

The best method available for further purification consists in dissolving the material in hot acetone. The resulting deep red solution was concentrated until it deposited bright yellow crystals of acetonate on cooling. These were filtered off and similarly recrystallized several times. Yield, about 21% theoretical.

A large amount of very soluble red material remained in the acetone, which was undoubtedly a mixture but consisted largely of hexaiodofluorescein. A portion of it was acetylated, purified as much as possible and analyzed.

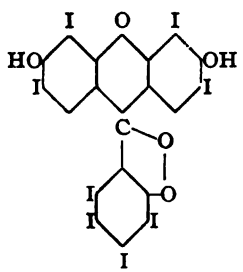
Subst. 0.2696; cc. 0.1 *N* $AgNO_3$, 13.99.
Calc. for $C_{24}H_{10}O_7I_6$: I, 64.99. Found: 65.86.

The material was not investigated further.

The yellow crystalline material from acetone was found to contain solvent of crystallization. Heated to constant weight at 120° it gave pure tetraiodoerythrosin.

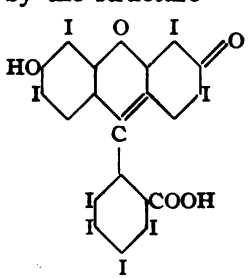
Subst. (I) 0.3344, (II) 0.1613; cc. 0.1 *N* $AgNO_3$, (I) 20.00, (II) 9.45.
Calc. for $C_{20}H_4O_5I_8$: I, 75.80. Found: (I) 75.90, (II) 74.36.

The compound freed from solvent of crystallization is a clear yellow and undoubtedly possesses the benzenoid structure



Tetraiodoerythrosin (yellow).

Prolonged heating at 140° causes it to go over to the dark red isomeric quinoid form represented by the structure



Tetraiodoerythrosin (red).

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Tetraiodoerythrosin dissolves in alkaline solution with a very deep red color and faint bluish fluorescence. The sodium and potassium salts are only slightly soluble in cold water, readily on warming. A dilute alkaline solution dyes silk direct giving an attractive shade of red.

When a dilute solution is acidified it throws down a light pink hydrate so unstable that it loses water when its aqueous suspension is boiled, the pink color then being replaced by a light yellow. It rapidly gives the yellow tetraiodoerythrosin when dried at 100°.

Tetraiodoerythrosin is insoluble in alcohol and glacial acetic acid and does not rearrange in the presence of either solvent to give the carbinol carboxylic acid. It dissolves easily in warm acetone from which it separates as a beautifully crystalline acetone addition product or acetonate.

Tetraiodoerythrosin Acetonate.—Pure tetraiodoerythrosin was dissolved in hot acetone. The pink solution on concentration gave bright yellow crystals which were carefully separated by filtration, using a hardened filter paper just previously washed with dilute nitric acid and distilled water. This was necessary, as the product is extraordinarily sensitive to alkalies, especially ammonia, so much so that an unwashed paper turned it red at once. Tetraiodoerythrosin should be much more delicate as an indicator for very dilute solutions than erythrosin itself.

The yellow crystals were dried to constant weight at room temperature in an atmosphere free from ammonia and then heated to 140°. The crystalline structure was thus lost.

Subst. 0.3769; weight lost 0.0200.
Calc. for $C_{20}H_4O_5I_8.C_3H_6O$: Acetone, 4.15. Found: 5.28.

The acetonate evidently contains one molecule of acetone. The fact that no such stable addition product forms with the lower iodinated fluorescein derivatives was utilized in the process of purification.

Tetraiodoerythrosin Diacetate.—Pure tetraiodoerythrosin was boiled gently for an hour with acetic anhydride containing some fused sodium acetate. The diacetate gradually separated out in the form of lemon-yellow crystals, that were purified by recrystallization from acetone. Yield, almost theoretical.

The pure product gave the following analysis:

Subst. (I) 0.1692, (II) 0.2643; cc. 0.1 *N* $AgNO_3$, (I) 9.53, (II) 14.77.
Calc. for $C_{24}H_6O_7I_8$: I, 71.32. Found: (I) 71 48, (II) 70.93.

The crystals are insoluble in ethyl acetate, readily soluble in acetone. They are unacted upon by 5% sodium hydroxide, but saponify very slowly on heating to boiling. The pure material gradually darkens above 200° with loss of iodine. The structure is benzenoid.

Tetraiodoerythrosin Dibenzoate.—Pure tetraiodoerythrosin was suspended in benzoyl chloride, 5 g. in 15 cc., and boiled gently for 30 minutes. The solution was then cooled and poured into an excess of alcohol. After

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washing the resulting precipitate of crude dibenzoate with alcohol to remove ethyl benzoate it was dissolved in hot chloroform. An equal volume of alcohol was added and the solution gradually concentrated to crystallization. Further recrystallizations from acetone after boiling with bone-black gave light yellow crystals of pure tetraiodoerythrosin dibenzoate.

Subst. (I) 0.2391, (II) 0.0851; cc. 0.1 *N* $AgNO_3$, (I) 12.43, (II) 4.42.

Calc. for $C_{34}H_{12}O_7I_4$: I, 65.60. Found: (I) 65.98, (II) 65.92.

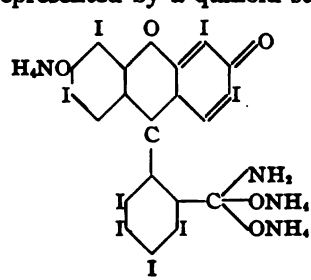
The dibenzoate decomposes without melting at about 300°. It is quite soluble in acetone and chloroform, insoluble in alcohol, and is not saponifiable by dilute sodium hydroxide. The extremely high formula weight of 1548 is notable, being surpassed by few if any compounds of known constitution. The yellow color demands a benzenoid structure.

Tetrammonium Salt.—A weighed sample of pure tetraiodoerythrosin in a porcelain boat was exposed to the action of dry ammonia until it reached constant weight. The yellow color changed to red at once, and ammonia was absorbed rapidly. Constant weight was reached after 12 hours, after which the sample was removed and heated at 120°. The following results were attained:

Subst. (I) 0.3748, (II) 0.6319. Gain in weight (I) 0.0179, (II) 0.0327. Loss in weight (I) 0.0170, (II) 0.0337.

Calc. for $C_{28}H_4O_5I_8.4NH_3$: NH_3, 4.84. Found: by gain (I) 4.77, (II) 4.94; by loss (I) 4.54, (II) 5.09.

The reaction undoubtedly takes place in steps, first adding two molecules of ammonia with molecular rearrangement analogous to tetraiodofluorescein and tetraiodoeosin. The third molecule may then add in much the same way as ammonia adds to phthalic anhydride, giving amine and hydroxyl groups on the carboxyl carbon. A fourth molecule of ammonia would then convert hydroxyl to ONH_4. The salt is a brilliant dark red and must be represented by a quinoid structure, probably as:



since it leaves the brick-red form of tetraiodoerythrosin on heating. This gives a ready means of converting the ordinary yellow benzenoid modification into the red quinoid form.

Silver Salt.—The silver salt was prepared by dissolving 5 g. of pure tetraiodoerythrosin in 600 cc. water containing 5 cc. concd. ammonium hydroxide. A slight excess of silver nitrate in solution was added which

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at once caused a separation of the monosilver salt as violet particles. The salt is very slightly soluble in an excess of ammonia, differing in this respect from the corresponding salts of tetraiodofluorescein and tetraiodoeosin. It was thoroughly washed with boiling water, filtered and dried to constant weight at 120°. Analysis for silver was made by treating for some hours with six-normal nitric acid in the cold, diluting, filtering and titrating silver with standard ammonium thiocyanate, using ferric alum as indicator.

Subst. (I) 0.3330, (II) 0.4622; cc. 0.1 *N* NH_4SCN, (I) 2.86, (II) 3.67.
Calc. for $C_{20}H_8O_5I_8Ag$: Ag, 7.45. Found: (I) 9.26, (II) 8.56.

High results are probably due to occluded or adsorbed silver nitrate. The silver salt of tertaiodoerythrosin possesses a very brilliant violet color. When treated with dilute nitric acid as above in the analysis it gives a reddish brown form of tetraiodoerythrosin.

Monomethyl Ether.—The methyl ether was readily obtained by vigorously shaking a solution of pure tetraiodoerythrosin in dilute sodium hydroxide solution with successive portions of dimethyl sulfate. A very dark red non-crystalline product separated out, easily soluble in acetone or chloroform, very slightly soluble in methyl or ethyl alcohol, and benzene. The substance is quite unstable, losing weight slowly even at 100° giving a dark brown residue. A sample dried to constant weight over calcium chloride gave the following data for methoxyl by the Zeissel method:

Subst. (I) 0.4728, (II) 0.0790. Weight AgI, (I) 0.0647, (II) 0.0106.
Calc. for $C_{20}H_2O_5I_8.OCH_3$: OCH_3, 1.11. Found: (I) 1.80, (II) 1.77.

This shows that it undoubtedly contains but one methoxyl radical.

Subst. (I) 0.2592; cc. 0.1 *N* $AgNO_3$, 13.85.
Calc. for $C_{21}H_6O_5I_8$: I, 75.01. Found: (I) 67.82.

The ether gives no color with cold dilute sodium hydroxide solution.

Summary.

1. Tetraiodoerythrosin, or octoiodofluorescein, has been made and isolated in pure condition.

2. It normally is yellow and in the benzenoid condition, but the colored quinoid form was obtained by warming the dry ammonia salt.

3. The acetonate was obtained as a stable addition product, forming yellow crystals containing one molecule of acetone.

4. These derivatives are all extremely sensitive to alkalies, especially to ammonia.

5. The diacetate is also yellow. It saponifies very slowly.

6. Tetraiodoerythrosin dibenzoate was obtained as light yellow crystals. It has the remarkable formula weight of 1548.

7. Dry ammonia gives a brilliant red tetrammonium salt, probably a derivative of the quinoid diammonium salt.

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8. The monosilver salt is a brilliant purple.

9. The monomethyl ether is deep fiery red.

10. A lower halogenated product consisting largely of hexaiodofluorescein was a constant by-product.

11. Spectroscopic studies of the above series will be reported upon in a later paper.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF PITTSBURGH.]

PHTHALIC ACID DERIVATIVES; CONSTITUTION AND COLOR, XI.[1] PHENOLTETRAIODOPHTHALEIN AND SOME OF ITS DERIVATIVES.

BY DAVID S. PRATT AND ASHER F. SHUPP.

Received October 17, 1917.

Phenolphthalein derivatives formed by condensing phthalic anhydride with phenol have offered especially interesting compounds for color studies ever since they were first prepared by Baeyer in 1871.[2] They also form one of our most valuable classes of indicators for acidimetry and alkalimetry. The preparation of phenoltetraiodophthalein with four atoms of iodine in the phthalic anhydride ring, and its derivatives containing in addition four atoms of bromine or iodine in the phenol residue, has been carried out to compare these phthaleins with known samples. It was anticipated that interesting and valuable properties might result from the increased unsaturation produced by such substitution, either from the standpoint of their hydrogen-ion concentration or their color.

Tetraiodophenolphthalein was probably obtained, although in an impure condition, by Rupp,[3] but he records very poor yields and colors which we did not obtain with the pure substance. He does not mention any of its derivatives.

Tetraiodophthalic anhydride can be prepared on a laboratory scale by slightly modifying the original method of Juvalta.[4]

Tetraiodophthalic Anhydride.—25 g. of phthalic anhydride and 90 g. of iodine were added to 100 cc. of commercial fuming sulfuric acid containing 50% free SO_3, and the mixture heated in an oil bath to 65° until the reaction neared completion. This stage can be judged by the cessation of bubbles of sulfur dioxide which continue to escape as long as iodination is proceeding. The temperature of the bath was then gradually raised to 175° and maintained for 15 minutes, then allowed to fall slowly. A long-neck round bottom liter flask was used with a condenser made

[1] THIS JOURNAL, 40, 198 (1918).

[2] *Ber.*, 4, 659 (1871).

[3] *Arch. Pharm.*, 249, 56 (1911).

[4] Ger., 50,177; see also Rupp, *Ber.*, 29, 1634 (1896).

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from a large test tube roughly fitting the neck of the flask and supported on a winding of asbestos cord to prevent the escape of sulfur trioxide and iodine. In preparing large amounts of tetraiodophthalic anhydride it is advisable to add the iodine in three portions of about 60%, 30% and 10%, waiting after each addition until the evolution of sulfur dioxide practically ceases. The preparation offered no special difficulties and good yields were always obtained.

The anhydride crystallized out of the strong sulfuric acid on cooling in the form of brilliant, yellow needles. The mixture was cooled to room temperature and slowly poured with stirring over cracked ice since considerable sulfur trioxide still remained in the acid and much heat was generated on dilution. The crystalline mass was repeatedly washed by decantation with warm water containing sulfur dioxide to remove sulfuric acid and iodine. The product so obtained is pure enough for use in making the phthalein. Yield, nearly theoretical. Further purification was achieved by dissolving in cold alkali and diluting. The dipotassium salt is fairly soluble in warm water, but care must be used to avoid excess alkalinity as iodine is removed with considerable ease. The practically neutral solution was heated to boiling by passing in steam and promptly acidified with hydrochloric acid. The steaming was continued one hour, during which the tetraiodophthalic acid gradually became finely crystalline. The solution was filtered hot and the pale yellow acid washed free from chlorides. It loses water very readily at 100° and goes over within a short time into the markedly deeper yellow-colored anhydride. Tetraiodophthalic anhydride may be recrystallized from nitrobenzene, better from phenol, in long, bright, yellow needles. It melts at 320–325° (corr.). Analysis by the lime combustion method:

Subst. (I) 0.1000, (II) 0.2244; cc. 0.1 *N* $AgNO_3$, (I) 6.10, (II) 13.79.
Calc. for $C_8O_3I_4$: I, 77.90. Found: (I) 77.42, (II) 78.00.

Phenoltetraiodophthalein.—A great deal of difficulty was encountered in causing tetraiodophthalic anhydride to condense with phenol. This appeared to be due largely at least to the insolubility of the former in hot phenol containing any dehydrating agent. The anhydride dissolved readily enough in melted phenol, but it was thrown out in long, yellow needles by the addition of even small amounts of sulfuric acid. These crystals did not redissolve and of course seriously reduced the yield of phthalein, at first practically to mere traces.

The difficulty was finally obviated by using a great excess of phenol and adding the sulfuric acid drop by drop as the reaction proceeded instead of all at the start as is customary. The question of temperature is also important if good yields are to be obtained. A typical preparation was as follows:

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100 g. of powdered tetraiodophthalic anhydride were dissolved in 800 g. of colorless freshly distilled phenol by warming to 160°. It is important that the anhydride be in solution before any acid is added. 120 g. of fuming sulfuric acid containing 13% free sulfur trioxide were then added drop by drop to the above solution contained in a 2-liter round bottom flask provided with a mechanical stirrer. The addition of sulfuric acid required about 1 hour. At no time did any anhydride crystallize out. The temperature was then raised to 170° and 400 g. more of the fuming sulfuric acid were added very slowly and with constant stirring. This addition of acid should require about 2 hours, and at no time should anhydride crystallize out. Small tests portions were now removed from time to time, placed on a slide and examined under the microscope. Uncondensed anhydride forms yellow, prismatic crystals on standing, especially if a trace of alcohol be added to the preparation on the slide. Heating should be continued until few, if any, such crystals form, ordinarily about 5 to 6 hours being required in all, including the preliminary heating.

The clear, deep red reaction product while still hot was poured into hot water contained in large cylinders and repeatedly washed by decantation with hot water. This wash water, on cooling, deposited crystals in large amount of oxysulfobenzide, a constant by-product of the reaction. It was not found practical to attempt removing such a large excess of phenol by distillation as is ordinarily done in phthalein condensations.

The residue contained the desired phthalein, tetraiodofluoran, and some unchanged tetraiodophthalic anhydride. It was dried in a water oven to insure the absence of tetraiodophthalic acid by converting it into anhydride, as the former is somewhat soluble in alcohol while the latter is not. The residue was extracted several times with ethyl alcohol in which the amorphous phthalein in readily soluble, then filtered from fluoran and anhydride. The alcoholic solution of phthalein contained some tarry products to remove which it was boiled with repeated portions of boneblack until it became a clear red. Slow concentration of this solution deposited well-formed yellow crystals of phenoltetraiodophthalein; rapid concentration gave an amorphous product. Yield, about 70 g.

The material was purified by recrystallization from alcohol and glacial acetic acid, using boneblack and long boiling. It melts at 239–45° when amorphous.

The pure product is lemon-yellow in color, readily soluble in ordinary organic solvents, such as alcohol, ether, chloroform, glacial acetic acid, etc., when in the amorphous form, but much less so when crystalline. Its structure is to be represented as

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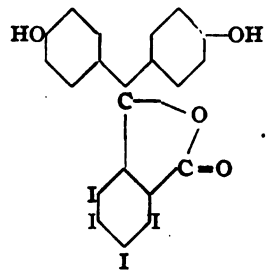

Subst. (I) 0.1974, (II) 0.2178; cc. 0.1 N $AgNO_3$, (I) 9.59, (II) 10.45.
Calc. for $C_{20}H_{10}O_4I_4$: I, 61.78. Found: (I) 61.70, (II) 61.90.

Phenoltetraiodophthalein undoubtedly owes its yellow color not to the presence of any quinoid arrangement of the molecule, but to the influence of four iodine atoms in shifting the absorption range into the visible spectrum. The proximity effect thus brought about by iodine in the anhydride is carried into the phthalein, provided the latter still conforms to the anhydride ring formation. The remaining carbonyl and anhydride oxygen are distinctly influenced chemically, as shown by the fact that phenoltetraiodophthalein does not react with hydroxylamine to give an oxime or with aniline to give an anilide, although both reactions are readily brought about with phenolphthalein itself. The color on spectroscopic investigation will, without question, correspond to that evidenced by the tetraiodophthalic anhydride. It was our intention to study the absorption spectra of all these compounds under a variety of conditions, in fact the principal theoretical points to be taken up were in this connection. The inability of London firms to make deliveries during the war of certain essential apparatus compels us to delay report on this portion of the work until a later paper.

Phenoltetraiodophthalein dissolves in alkali with a deep red color somewhat similar to that of ordinary phenolphthalein but lacking the purple tone. A weighed sample of the phthalein exposed to ammonia gas either dry or moist, failed to change color and did not gain in weight. Evidently no salt is formed under these conditions.

Tetraiodofluoran.—The residue that remained after extracting the phthalein with alcohol contained unchanged tetraiodophthalic anhydride and tetraiodofluoran. The former was removed with warm dilute alkali as the disodium salt and the final residue dissolved in hot glacial acetic acid. The solution was boiled with boneblack, and deposited, on concentration, yellow crystals of tetraiodofluoran. It is insoluble in alcohol, chloroform, acetone, ethyl acetate, phenol, nitrobenzene, and alcoholic alkali, very sparingly in acetic acid. The pure compound decomposes at about 319° (corr.).

Subst. (I) 0.1390, (II) 0.1414; cc. 0. 1 N $AgNO_3$, (I) 6.89, (II) 7.02.
Calc. for $C_{20}H_8O_3I_4$: I, 63.16. Found: (I) 62.91, (II) 63.01.

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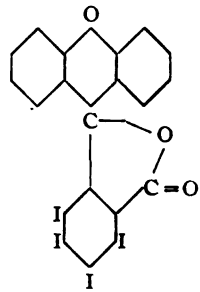
The structure of the tetraiodofluoran is



Phenoltetraiodophthalein Diacetate.—The acetate was prepared by boiling for 1 hour a mixture of 5 g. of pure phenoltetraiodophthalein and 3 g. of fused sodium acetate in 15 cc. of acetic anhydride. The reaction product was poured on ice, filtered off and thoroughly washed. After drying it was dissolved in benzene containing a little acetic anhydride and boiled with boneblack for 4 days. The solvent was distilled off, and the acetate recrystallized from absolute methyl alcohol. Further crystallization from ethyl alcohol caused no change in the melting point of 230° (corr.). Yield, about 60%. Analysis:

Subst. (I) 0.2961, (II) 0.2116; cc. 0.1 *N* $AgNO_3$, (I) 13.06, (II) 9.32.
Calc. for $C_{24}H_{14}O_6I_4$: I, 56.04. Found: (I) 55.98, (II) 55.90.

The diacetate forms light yellow crystals similar in color to the phthalein. It is very readily saponified by aqueous alkali in the cold.

Phenoltetraiodophthalein Dibenzoate.—The benzoate may be prepared by boiling pure phenoltetraiodophthalein for an hour with benzoyl chloride. A rather more satisfactory method is to dissolve the phthalein in dilute alkali and shake the solution vigorously with successive small portions of benzoyl chloride. Alkali should be added at intervals to prevent the solution becoming acid. The completion of the reaction is shown by the disappearance of the red color.

The product, after thorough washing with dilute alkali, followed by water and finally alcohol, was crystallized from benzene. The melting point of 236° (corr.) was not altered by dissolving in chloroform and throwing out by the addition of alcohol.

Subst. (I) 0.1501, (II) 0.2202; cc. 0.1 *N* $AgNO_3$, (I) 5.82, (II) 8.70.
Calc. for $C_{34}H_{18}O_6I_4$: I, 49.29. Found: (I) 49.21, (II) 50.10.

The dibenzoate crystallizes in light yellow needles, difficultly soluble in alcohol and ether; easily in benzene, acetone or chloroform.

Phenoltetraiodophthalein Dimethyl Ether.—Pure phenoltetraiodophthalein was dissolved in alkaline solution and shaken vigorously with successive small portions of dimethyl sulfate taking care to avoid rise in

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temperature. The red color gradually disappeared as the ether precipitated out. The most satisfactory solvent for purification proved to be ethyl alcohol, from which, on very slow evaporation, the ether was obtained crystalline.

Subst. (I) c.1593, (II) 0.2112; cc. 0.1 *N* $AgNO_3$, (I) 7.58, (II) 10.00.
Calc. for $C_{22}H_{14}O_4I_4$: I, 59.74. Found: (I) 60.39, (II) 60.09.

The dimethyl ether forms deep canary-yellow crystals which melt at 221° (corr.). It is quite soluble in chloroform, benzene, acetone, only slightly so in alcohol or ether. The structure is correctly represented by the benzenoid form, the yellow color being normal. The isomeric quinoid ether ester was not obtained.

Dinitrophenoltetraiodophthalein.—A suspension of 10 g. pure phenoltetraiodophthalein in 220 g. of sulfuric acid (sp. gr. 1.84) was heated to 90° for one hour with vigorous mechanical stirring, during which the deep red color of the suspended phthalein turned to a brick red. The material was cooled to room temperature and a mixture consisting of 33 g. of nitric acid (sp. gr. 1.43) and 40 g. of sulfuric acid (sp. gr. 1.84) was slowly added with stirring. After the nitrating acid had all been added the temperature was raised to 90° and maintained with constant stirring until a test sample dropped into dilute alkali showed only a few particles turning red. Prolonged heating would be necessary to cause complete nitration of these particles, and such is not desirable, as tars are readily produced and are exceedingly difficult to remove.

The reaction mixture was cooled and poured into water. The precipitated crude phthalein was dissolved in dilute alkali and reprecipitated by adding dilute hydrochloric acid. It was dried and extracted with ethyl alcohol to remove unchanged phenoltetraiodophthalein, then treated for a few minutes with warm acetone. The dinitro product is readily soluble in warm acetone while the tetranitro derivative is not.

Dinitrophenoltetraiodophthalein is soluble in hot ethyl alcohol, cold chloroform, ethyl acetate and acetone. It crystallizes only when pure, then giving yellow needles which decompose about 311–312° (corr.). Yield, 20%.

Subst. (I) 0.0447, (II) 0.1100; cc. 0.1 *N* $AgNO_3$, (I) 1.97, (II) 4.81.
Calc. for $C_{20}H_8O_8N_2I_4$: I, 55.67. Found: (I) 55.93, (II) 55.50.

The dinitrophenoltetraiodophthalein dissolves in dilute alkaline solution with a deep orange-yellow color. The distribution of the two nitro groups was not fixed, but it is more than probable that each phenol residue contains one nitro group in a position ortho to the hydroxyl.[1] This would give the structure

[1] THIS JOURNAL, 38, 2486 (1916).

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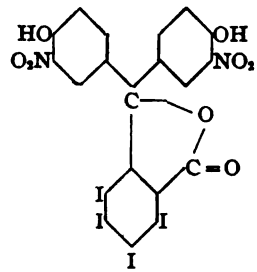

Discussion of probable structure in the yellow alkaline solution is reserved until spectroscopic data are available.

Dinitrophenoltetraiodophthalein Diacetate.—The nitrophthalein is easily decomposed by heat so that special care must be used in acetylating it. A solution of pure dinitrophenoltetraiodophthalein in acetic anhydride containing a little fused sodium acetate was warmed for 15 minutes on a water bath. The reaction product was poured into cold water, filtered and washed. It was then purified by treating an acetone or chloroform solution with enough alcohol to cause crystallization on standing. Yield, about 60%.

Subst. (I) 0.2983, (II) 0.2882; cc. 0.1 *N* $AgNO_3$, (I) 12.26, (II) 11.94.
Calc. for $C_{24}H_{12}O_{10}N_2I_4$: I, 50.98. Found: (I) 52.16, (II) 52.58.

The pure product forms deeply yellow crystals sparingly soluble in alcohol even on heating, easily soluble in acetone and chloroform. Melting point 281° (corr.).

Tetranitrophenoltetraiodophthalein.—In the purification of dinitrophenoltetraiodophthalein there remained some yellow material insoluble in warm acetone. This was finally dissolved by long boiling with an excess of acetone. Concentration caused the substance to deposit slowly in clear, yellow crystals.

Subst. (I) 0.1048, (II) 0.1138; cc. 0.1 $AgNO_3$, (I) 4.25, (II) 4.66.
Calc. for $C_{20}H_8O_{12}N_4I_4$: I, 50.67. Found: (I) 51.47, (II) 51.97.

The presence of four nitro groups tended to cause the halogen determinations made in this way to run high, due to the formation of cyanides. For this reason the phthalein was dissolved in glacial acetic acid and reduced with zinc dust, and finally analyzed for nitrogen by the Kjeldahl method:

Subst. (I) 0.2215, (II) 0.0387; cc. 0.1 *N* HCl, (I) 8.55, (II) 1.68.
Calc. for $C_{20}H_8O_{12}N_4I_4$: N, 5.59. Found: (I) 5.33, (II) 6.08.

The material is evidently tetranitrophenoltetraiodophthalein. The yellow crystals decompose at about 311° (corr.). They are difficultly soluble in acetone and alcohol, readily in dilute alkaline solution with a yellow color, bordering on orange. The following structure should be assigned to the compound:

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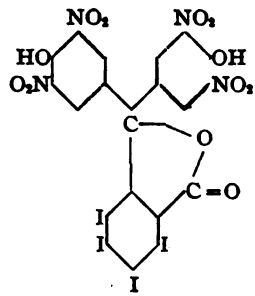

Tetrabromophenoltetraiodophthalein.—Tetrabromophenoltetraiodophthalein contains two bromine atoms in each phenol ring in addition to the iodone in the phthalic anhydride residue. It was made by dissolving 10 g. of pure phenoltetraiodophthalein in 150 cc. ethyl alcohol, and adding to this solution while boiling about 7 cc. of bromine in 50 cc. of glacial acetic acid. The reaction was complete in 15 minutes, and since the product was only slightly soluble in alcohol, it crystallized out as it formed. Yield, theoretical.

The crude material was recrystallized once from alcohol and obtained pure in yellow crystals melting at 311–312° (corr.). Analysis was made by the lime combustion method, weighing the combined halides in addition to titrating with standard ammonium thiocyanate.

Subst. (I) 0.1827, (II) 0.1822; cc. 0.1 *N* $AgNO_3$, (I) 12.31, (II) 12.49. Weight AgI + AgBr: (I) 0.2616, (II) 0.2653.

Calc. for $C_{20}H_6O_6Br_4I_4$: Br, 28.13; I, 44.63. Found: (I) Br, 27.26; I, 43.30; (II) Br, 27.68; I, 43.95.

Tetrabromophenoltetraiodophthalein is slightly soluble in hot alcohol, more so in ether, acetone and benzene, but difficult to obtain crystalline from any except the first. The compound indicates by its normal yellow color that it possesses the benzenoid formation, in which the bromine atoms are undoubtedly ortho to the hydroxyl groups. Dry ammonia has no effect on the phthalein, but aqueous alkali dissolves it with a clear deep blue color very similar to that given by thymolphthalein.

Tetrabromophenoltetraiodophthalein Diacetate.—The diacetate was made in an analogous manner to that used in making phenoltetraiodophthalein diacetate except that the time of boiling was reduced to 30 minutes. The crude product in benzene was boiled with boneblack, and finally obtained pure from chloroform by the gradual addition of alcohol. It forms bright yellow crystals which melt at 285° (corr.).

Subst. (I) 0.1990, (II) 0.1924; cc. 0.1 *N* $AgNO_3$, (I) 12.70, (II) 12.25. Weight of AgI + AgBr: (I) 0.2716, (II) 0.2587.

Calc. for $C_{24}H_{10}O_6Br_4I_4$: Br, 26.17; I, 41.56. Found: (I) Br, 26.13; I, 41.50; (II) Br, 25.41; I. 40.43.

Tetrabromophenoltetraiodophthalein Dibenzoate.—The benzoate was

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readily obtained by the Schotten-Baumann reaction as in the preceding case. The product so made was similarly purified and finally crystallized from hot chloroform by the addition of alcohol. Yield, about 80%.

Subst. (I) 0.2184, (II) 0.2110; cc. 0.1 *N* $AgNO_3$, (I) 12.91, (II) 12.33. Weight of AgBr + AgI: (I) 0.2752, (II) 0.2615.

Calc. for $C_{34}H_{14}O_6Br_4I_4$: Br, 24.76; I, 37.73. Found: (I) Br, 24.05; I, 38.20; (II) Br, 24.08; I, 38.24.

The dibenzoate forms yellow crystals melting at 213–215° (corr.), soluble in acetone, benzene, ethyl acetate and chloroform, slightly soluble in alcohol.

Tetrabromophenoltetraiodophthalein Dimethyl Ether.—The dimethyl ether was made by shaking an alkaline solution of the pure phthalein with dimethyl sulfate until the blue color disappeared. The dried precipitate so obtained was dissolved in chloroform, and the solution mixed with ethyl alcohol in about equal amount and concentrated by distillation until the ether crystallized out on cooling. The addition of alcohol to the hot chloroform solution does not throw down the ether in crystalline form, as was the case with the acetate and benzoate.

Subst. (I) 0.2789, (II) 0.2193; cc. 0.1 *N* $AgNO_3$, (I) 20.76, (II) 15.13. Weight of AgBr + AgI: (I) 0.4236, (II) 0.3157.

Calc. for $C_{22}H_{10}O_4Br_4I_4$: Br, 27.42; I, 43.56. Found: (I) Br, 27.52; I, 43.71; (II) Br, 26.87, (II) I, 42.67.

The dimethyl ether gave lemon-yellow crystals melting at 255° (corr.). It is readily soluble in acetone, benzene and ethyl acetate, much less so in alcohol.

Tetraiodophenoltetraiodophthalein.—This respresents the maximum iodine substitution possible in phenolphthalein. The product was made by dissolving 15 g. of pure phenoltetraiodophthalein in a slight excess of dilute alkali, cooling with ice, and gradually adding a solution of 30 g. of iodine in potassium iodide solution. The cold mixture was stirred mechanically during the addition of iodine, and kept alkaline by supplying sodium hydroxide to neutralize the hydriodic acid liberated by the reaction.

About $1^1/_2$ hours were allowed for completion of the reaction, during which the red color was replaced by a greenish blue. The crude phthalein was precipitated by acidification, well washed with dilute potassium iodide solution to remove excess iodine, followed by boiling water, and dried. It was then treated with cold chloroform to remove unchanged phenoltetraiodophthalein and dissolved in boiling alcohol. Slow concentration of the alcoholic solution and long standing gave the pure compound in deep yellow crystals. Yield, about 50%.

Subst. (I) 0.3792, (II) 0.2019; cc. 0.1 *N* $AgNO_3$, (I) 22.96, (II) 12.17.

Calc. for $C_{20}H_8O_4I_8$: I, 76.60. Found: (I) 76.85, (II) 76.50.

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Tetraiodophenoltetraiodophthalein consists of over 75% iodine and still preserves its distinct character as a phthalein. The pure compound from alcohol forms clear, yellow crystals which decompose with loss of iodine at about 285° (corr.). It is difficultly soluble in ordinary solvents, especially when in the crystalline form. Dry ammonia does not give a salt, but the phthalein is readily soluble in aqueous alkali with a royal blue color.

Tetraiodophenoltetraiodophthalein Acetate.—10 g. of pure tetraiodophenoltetraiodophthalein and an equal weight of fused sodium acetate were boiled for 30 minutes with 40 cc. of acetic anhydride. The phthalein remained in suspension but was gradually acetylated. The products were poured into cold water and the acetate washed and dried. It was recrystallized until pure from chloroform by precipitating with alcohol. Yield, 60%.

Subst. (I) 0.1501, (II) 0.1201; cc. 0.1 *N* $AgNO_3$, (I) 8.55, (II) 6.81.
Calc. for $C_{24}H_{10}O_6I_8$: I, 72.03. Found: (I) 72.29, (II) 71.97.

The diacetate is difficultly soluble in alcohol, readily in acetone, ethyl acetate and benzene. It forms pale yellow crystals melting at 288° (corr.).

Tetraiodophenoltetraiodophthalein Dibenzoate.—The dibenzoate was made by the Schotten-Baumann reaction and purified in the same way as the previous benzoates. Yield, 80%. A sample of the purified product gave the following analysis:

Subst. (I) 0.2223, (II) 0.3168; cc. 0.1 *N* $AgNO_3$, (I) 11.58, (II) 16.52.
Calc. for $C_{34}H_{14}O_6I_4$: I, 66.21. Found: (I) 66.11, (II) 66.18.

The dibenzoate forms light yellow crystals difficultly soluble in alcohol and ether, easily in benzene, chloroform, and acetone. The pure substance melts at 202–3° (corr.).

Tetraiodophenoltetraiodophthalein Dimethyl Ether.—The dimethyl ether was made in exactly the same way as the corresponding ethers previously mentioned. Acetone or chloroform are the best solvents, slow evaporation of either giving well-formed pale yellow crystals, decomposing at about 295–297° (corr.). Yield, 40%.

Subst. (I) 0.0968, (II) 0.1053; cc. 0.1 *N* $AgNO_3$, (I) 5.75, (II) 6.19.
Calc. for $C_{22}H_{12}O_4I_8$: I, 75.01. Found: (I) 75.39, (II) 74.61.

Summary.

1. Pure phenoltetraiodophthalein has been obtained in the form of yellow crystals, soluble in alkaline solution with a deep red color.
2. The benzenoid diacetate, dibenzoate and dimethyl ether have all been prepared in crystalline form.
3. Tetraiodofluoran was isolated as a by-product.
4. Dinitrophenoltetraiodophthalein and its diacetate were made.
5. Tetranitrophenoltetraiodophthalein was formed with the dinitro

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product and purified. Both of these compounds are yellow and dissolve in alkali with an orange-yellow color.

6. Tetrabromophenoltetraiodophthalein results from the bromination of phenoltetraiodophthalein. It is a yellow crystalline product, soluble in alkali with a deep blue color.

7. The corresponding diacetate, dibenzoate, and dimethyl ether were made.

8. Tetraiodophenoltetraiodophthalein is a yellow crystalline substance soluble in alkaline solution with a deep blue.

9. Its diacetate, dibenzoate, and dimethyl ether are all yellow.

10. The absorption spectra and theoretical discussion of these substances will be reported upon in a later paper.

PITTSBURGH, PA.

THE MOLECULAR MECHANISM OF COLLOIDAL BEHAVIOR.

I. THE SWELLING OF FIBRIN IN ACIDS.

BY RICHARD C. TOLMAN AND ALLEN E. STEARN.

Received October 22, 1917.

In previous articles,[1] one of the authors has discussed the general behavior of colloidal systems from a *thermodynamic* point of view. In a series of articles, of which this is to be the first, it is proposed to subject a number of typical colloidal systems to an intensive study from a *molecular* or *microscopic* point of view. Such studies will provide a much more intimate and complete basis for the explanation and prediction of colloidal behavior than can be done on the basis of thermodynamic considerations alone. No special attempt will be made to preserve any logical order of publication for these articles.

The swelling of protein colloids in acid and in alkaline solution and the decrease in swelling produced by the addition of neutral salts is a matter, both of great physiological and pathological interest, and has been particularly studied by Fischer[2] in his important experimental and clinical researches. The purpose of the present work is to investigate the molecular mechanism by which such swellings and reductions in swelling are brought about. We may say in advance, that our experimental results are in accord with the theory that a colloidal gel, such as a piece of fibrin covered by water, is a fibrous sponge-like structure with many minute pores or pockets which are themselves full of water. The addition of acid or alkali is followed by the adsorption, respectively, of hydrogen or hydroxide ion on the surface of these pockets and a consequent increase in their size owing to electrostatic repulsion, the increase in size being accompanied, of course, by imbibition of solution. The further addition

[1] Tolman, THIS JOURNAL, 35, 307, 317 (1913); *Science*, 44, 565 (1916).

[2] Fischer, "Edema and Nephritis," New York, 1915.

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of a neutral salt to the solution is followed by a decrease in swelling since the ions of the added salt will arrange themselves in such a way as to neutralize the original electrostatic repulsion.

Experimental Methods.

In the work which is now to be described, our method of attack has been to determine the swelling of a typical and easily handled protein colloid, blood fibrin, in solutions of hydrochloric, nitric, sulfuric, acetic, and formic acids of varying concentrations and to determine at the same time the amount of acid adsorbed from the solution by the fibrin. We have, furthermore, made similar measurements with solutions of sodium chloride and mixed solutions of acid and sodium chloride.

The Materials.—The same sample of blood fibrin was used throughout the work. It was purified before use by grinding to a coarse powder and washing repeatedly with 0.1 N hydrochloric acid. It was then washed with distilled water until the acid concentration in the wash water had fallen to less than 0.0001 N, and the water drained off. It was then dried in a current of warmed air for several days to volatilize any remaining acid.

The acids and salt used were ordinary "C. P." reagents.

The Swellings.—In order to determine the swellings of the fibrin, a number of special test tubes were procured of a *uniform cross section* of one-half inch and with *flat bottoms*. Uniform samples of 0.3 g. each of the powdered fibrin were put in these tubes and 15 cc. of the desired solution added and the heights to which the fibrin rose compared with a water control. In general, the samples were allowed to stand twenty-four hours with occasional shaking, this being long enough for the final height to be attained. (On further standing, a slight settling usually occurred.)

The Adsorption.—The adsorption experiments were carried out in glass "finger bowls," usually 2 g. of fibrin being used and 100 cc. of solution added, the materials thus being in the same proportions as in the swelling experiments. The solutions were allowed to stand twenty-four hours with occasional stirring and then analyzed. The acids were titrated against sodium hydroxide, standardized with oxalic acid, and the sodium chloride determined by Volhard's method, using ferric nitrate as an indicator. While the adsorption was taking place the finger bowls were kept covered with closely fitting cover glasses, which did not permit enough evaporation seriously to affect the results. In further work glass-stoppered bottles will be used.

The number of mols of acid A *adsorbed per g. of fibrin* was calculated by the following formula:

$$A = \frac{(C_0 - C)V}{W} \qquad (1)$$

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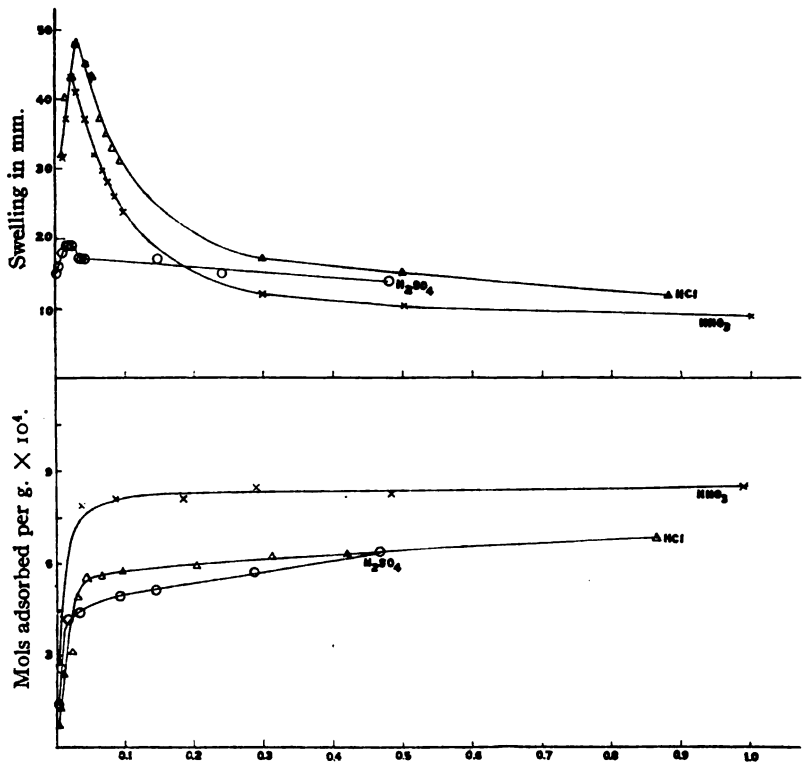
where C_0 is the original concentration of the solution in mols per liter, C the reduced concentration after the adsorption has taken place, V the volume in liters of solution employed, and W the weight of fibrin in grams.

Experimental Results and Discussion.

The Strong Acids.—The three *upper* curves in Fig. 1 show the swelling of fibrin in different concentrations of hydrochloric, nitric and sulfuric acids. The ordinates give the height in mm. to which the fibrin rose and the abscissas give the concentrations C in mols per liter of the surrounding



Concentration ~~of NaCl~~ in mols per liter.

Fig. 1.

solution (after adsorption has taken place). The sharp maximum of swelling at a low concentration of acid is to be noticed. The three *lower* curves in Fig. 1 show the adsorption of acid by the fibrin. The ordinates give the number of mols of acid adsorbed per g. of fibrin and the abscissas give the concentrations of solution plotted on the same scale as above. Actual observations are indicated in these plots by points, and considering the lack of precision and reproducibility in colloidal behavior, we believe that the smooth curves give a reasonably good representation of the facts.

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It will be noticed that the adsorbed acid at first increases very rapidly with the concentration and then more slowly finally approaching nearly a constant value. This accords with the usual behavior of adsorption curves, and could be explained by the assumption that the adsorption proceeds until the surface in question finally becomes coated with a layer of adsorbed substance one molecule thick and adsorption then ceases.[1]

In the particular case at hand, we believe that the walls of the pockets or pores in the interior of the fibrin have a great affinity for hydrogen ion, or in accordance with the amphoteric nature of the amino acids composing the fibrin, also for hydroxide ion. As soon as a little acid is added, hydrogen ion is at once adsorbed on the surface of these pockets, the corresponding anions being held by electrostatic attraction in the neighborhood of the adsorbed hydrogen, to form a "double layer." The adsorption of hydrogen ion continues until about 0.0006 to 0.0008 mol of hydrogen ions per g. of fibrin have been adsorbed, the surface of the pockets then being pretty well covered. Further addition of acid to the solutions then results merely in increasing the concentration of acid in the interior of the pockets and does not appreciably increase the amount adsorbed.

The course followed by the adsorption can apparently be used to explain the course taken by the swelling. On the first additions of acid when the amount of adsorbed hydrogen ion is increasing rapidly, the swelling also increases rapidly, owing to the electrostatic repulsion which forces the walls of the pockets further apart with the imbibition of solution. Later additions of acid, however, serve to increase the concentration of the acid in the interior of the pockets without appreciably raising the amount of adsorbed hydrogen ion, and this is accompanied by a decrease in swelling since, in accordance with electrostatic theory, the ions in the interior of the pocket will evidently tend to arrange themselves in such a way as to neutralize the original electrostatic repulsion. We believe that this accounts for the decided maximum of swelling in the particular range of concentration where the amount of adsorbed acid ceases to rise rapidly.

The Weak Acids.—The two upper curves in Fig. 2 show the *swelling* of fibrin in different concentrations of acetic and formic acids and the two lower curves show the *adsorption* of the acid. For purposes of easy comparison these curves are plotted on the same scale as in the previous figure for the strong acids.

Especial attention may be called to the fact that there is no *maximum* swelling in the case of the weak acids. In terms of our theory, this arises because we are working with a weak electrolyte and there is only a small concentration of ions in the interior of the pockets whose electrical fields

[1] See for example Langmuir, THIS JOURNAL, 38, 2221 (1916).

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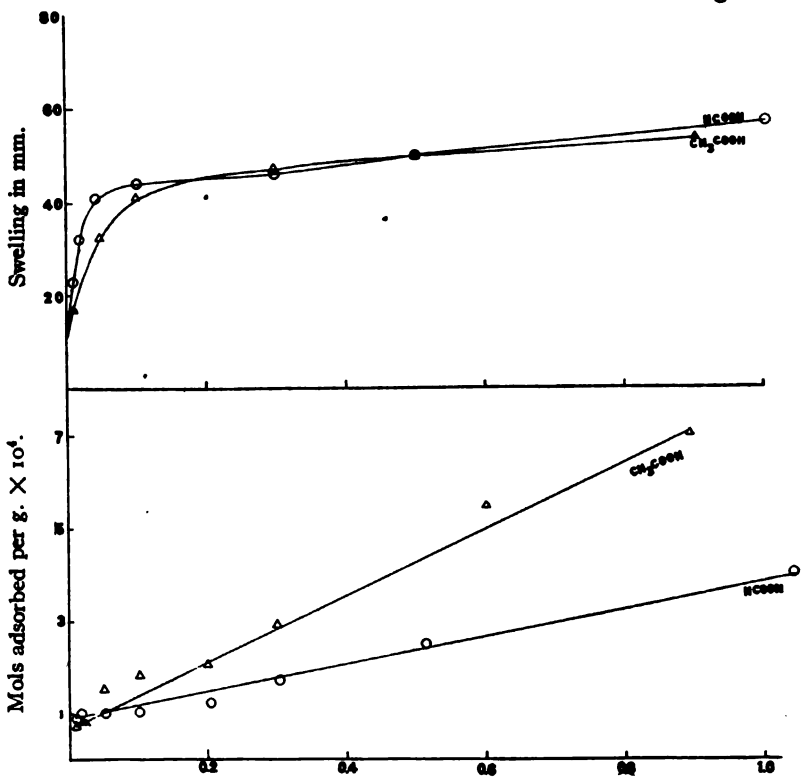
are available for neutralizing the electrostatic repulsion of the adsorbed ions.

This difference between the behavior of weak and strong acids becomes very noticeable if we go to high concentrations. Since there is no strong electrolyte present to bring about a reduction of swelling, we found at high concentrations of acetic acid (say, from 0.5 N on), that the fibrin was swollen into a sticky gelatinous mass. Moreover, we found that the amount of adsorbed acid continued to increase with increasing concen-



Concentration in mols per liter.
Fig. 2.

tration, until finally with the N acetic acid we got in the neighborhood of 0.006 mol of acid adsorbed per g. of fibrin as against the maximum adsorption with hydrochloric acid apparently of about 0.0007 mol per g. We are inclined to believe that this is due to the fact that the continued swelling leads to a sort of opening up of the pockets or separation of fibers which furnishes new surfaces where adsorption can take place.

Mixed Acid and Salt Solutions.—We have explained the occurrence of a maximum swelling in the case of strong acids by assuming, at the

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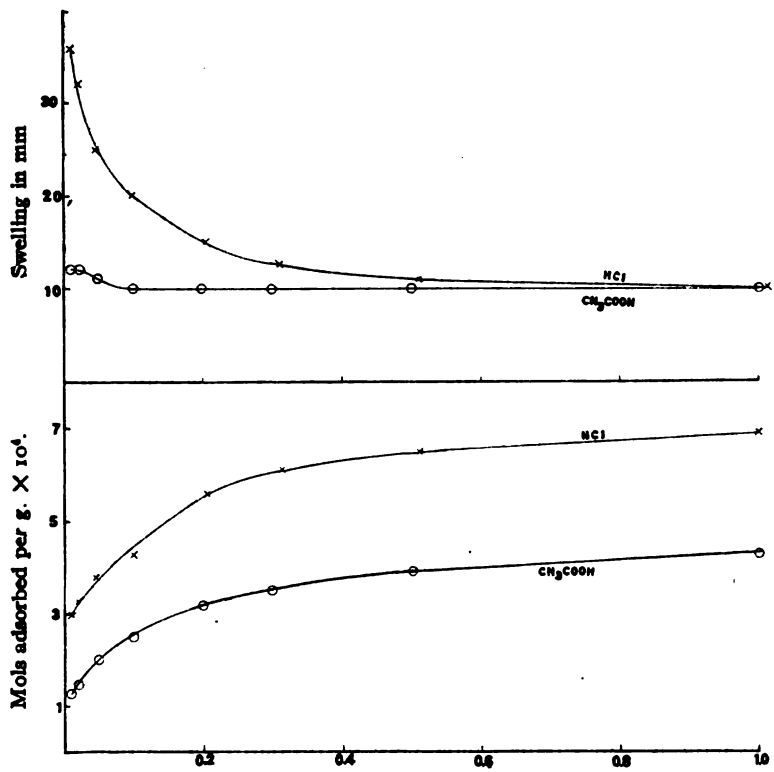
higher concentrations, that the strong electrolyte in the interior of the pockets furnishes ions which tend to arrange themselves in such a way as to neutralize the repulsive forces exerted by the adsorbed ions. If this is the case, we should obtain a check on our theory by investigating the behavior of fibrin in acid solutions to which strong *neutral* electrolytes are added.

This behavior in mixed solutions is given in Fig. 3, where the two upper curves give the *swelling* of fibrin in solutions which were made up



Concentration of NaCl in mols per liter.

Fig. 3.

0.015 *N*, respectively, with hydrochloric and acetic acids, and with increasing concentrations of sodium chloride as indicated by the abscissas of the plot. It will be noticed in agreement with our theory that increasing the concentration of the added salt reduces the swelling produced by the acid until at the higher concentrations the swelling is even less than that in pure water in the case of both the acids.

We must also call attention to the important effect which the added salt has upon the *adsorption* of acid. This is shown by the two lower curves

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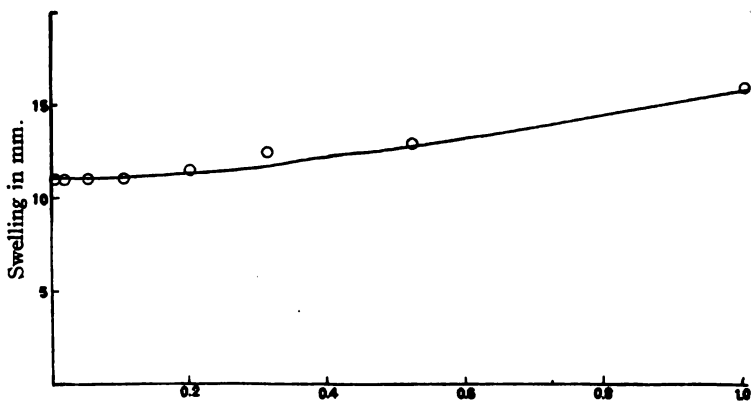
in Fig. 3. It will be seen that increasing the concentration of *salt* increases the adsorption of *acid*. This also seems explainable in terms of our concepts. As soon as any hydrogen ion is adsorbed this sets up a directed electric field which, as we have already pointed out, leads to an increase in size of the pockets, but will also evidently have the effect of discouraging further adsorption. The neutralization of this field by the ions of the neutral salt would increase the adsorption, as actually turns out to be the experimental fact. (It should be noticed that sodium chloride increases the adsorption of acetic acid as well as of hydrochloric acid, thus ruling out the common ion effect as an explanation.)

Pure Salt Solutions.—We may now finally call attention to the behavior of fibrin in pure sodium chloride solutions. There is, of course, no great swelling in such solutions since our theory does not lead us to expect any selective adsorption either of sodium or chloride ion. This is shown by the curve in Fig. 4, where it will be seen that even at N concentration



Concentration of NaCl in mols per liter.

Fig. 4.

the swelling is still small, what there is, probably being due to a slight specific adsorption either of sodium or chloride ion.

Analysis of the solutions gave further evidence that there is no particular adsorption of the ions of sodium chloride, since the concentration of the solutions actually rose when they were placed in contact with fibrin, thus showing that there is more tendency for water to be adsorbed by the fibrin than for sodium chloride. In fact, analyses of this kind would permit us to calculate the amount of adsorbed water, making, of course, the somewhat improbable assumption that absolutely no salt at all is adsorbed. In some further work now in progress it is hoped to obtain more satisfactory information as to the amount of adsorbed water, using sugar as the non-adsorbed reference substance.

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Conclusion.

We believe the data and discussion which we have presented are sufficient to make our theory as to the molecular mechanism of protein swelling highly probable. A brief restatement of the theory will not be out of place.

(1) In accordance with their amphoteric nature protein colloids have a marked tendency to adsorb hydrogen ion from acid solutions and hydroxide ion from alkaline solutions.

(2) In an acid solution, the adsorbed hydrogen ions, together with a corresponding number of anions, form a "double layer" on the walls of the pockets or pores in the interior of the gel and this leads to swelling and imbibition of water by electrostatic repulsion.

(3) The addition of a strong electrolyte to such a swollen colloid, either a neutral salt or excess of the strong acid which caused the original swelling, will furnish ions in the interior of the pockets which will tend to arrange themselves so as to neutralize the electrical fields of the adsorbed layer and thus bring about a reduction of swelling.

(4) The addition of a neutral salt to an acid solution tends to neutralize the electrical field of the adsorbed acid, and hence makes it easier for more acid to get to the surface of the pockets, thus leading to increased adsorption.

(5) It must be further noticed that in accordance with our theory, salts with polyvalent ions should be more effective in reducing swelling than salts with univalent ions; since, for example, a bivalent ion will take up no more room than a univalent ion, but will be twice as effective in neutralizing an existing electric field. That salts with polyvalent ions are the most effective in producing dehydration has been shown, particularly by the extensive work of Fischer.[1]

The conclusions which we have drawn are largely based on the experimental data for fibrin which we have presented in this paper. We have also made some experiments, however, on slabs of gelatin, and obtained an adsorption curve for gelatine and hydrochloric acid quite similar to the one for fibrin. We may further call attention to the similar adsorption curves obtained by Herzog and Adler,[2] using powdered hide and the work of Procter[3] using gelatin.

We have spoken throughout the article of the adsorption of hydrogen ion (or hydroxide ion). We have purposely made no assumptions, however, as to the molecular nature of this adsorption. Our theory would be equally applicable, if the adsorption process should lead to a fairly uniform coating of ions over the whole of the exposed surface, or, on the other hand, if the hydrogen ion should only tend to go on to the protein

[1] *Loc. cit.*

[2] *Kolloid-Z.*, supplement March, 1908, p. 111.

[3] *J. Chem. Soc.*, 105, 313 (1914).

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molecule at special points, where there is a particularly strong stray field, say, for example, where the amino and acid groups of the amino acids come together. It may be that later work will throw light on this point.

URBANA, ILL.

[CONTRIBUTION FROM THE EICHBERG LABORATORY OF PHYSIOLOGY IN THE UNIVERSITY OF CINCINNATI.]

ON THE SWELLING OF GELATIN IN POLYBASIC ACIDS AND THEIR SALTS.[1]

BY MARTIN H. FISCHER AND MARIAN O. HOOKER.

Received October 31, 1917.

I. Introductory.

It is now safe to conclude that the amount of water absorbed by any living cell, organ or organism, is essentially dependent upon its content of hydrophilic colloids and the state of these. As proof for this may be cited the complete analogy which exists between the laws governing the absorption of water by protoplasm and those governing the same phenomenon as observed in various simple colloids—more particularly the proteins—under physiological and pathological conditions.[2] On such a colloid-chemical basis it is now easy to account for the fairly constant amount of water held by living cells and tissues normally and so to explain, for example, their so-called normal "turgor." But under pathological conditions both in plants and in animals this normal degree of hydration may be much increased, when we have before us the "excessive turgor" characteristic of various plant diseases, or the edema of the animal pathologists as this involves individual cells, organs, or the body as a whole. Edema may, in other words, be defined as a state of excessive hydration of the body colloids, while as "causes" of the edema may be cited substances or conditions which under the circumstances prevailing in living protoplasm are capable of increasing its water holding powers to beyond the normal limits.

In connection with this problem of the "causes" of edema a study of the conditions which under laboratory circumstances increase the hydration capacity of different colloids has again yielded valuable hints as to the nature of those which are active in living protoplasm. Among the substances thus active so far as the proteins are concerned, acids occupy a first place; important, too, are the amines; while effective in this regard,

[1] A preliminary statement of the results detailed in this paper appeared in *Science*, 46, 189 (1917).

[2] Martin H. Fischer, "Physiology of Alimentation," 250, 268, New York, 1917; *Am. J. Physiol.*, 20, 339 (1907); *Pflüger's Arch.*, 124, 69 (1908); for a running account and detailed references, see Fischer, "Edema and Nephritis," 2nd Ed., New York, 1915.

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though not, perhaps, of much physiological or pathological importance, are pyridine and urea. In other words, we may expect an edema to result whenever in any living tissue there occurs an abnormal production or accumulation of these substances.

There has been much that is foolish written against these simple conclusions. Insofar as many of these criticisms rest upon a misreading or an actual violation of what we have written we shall not trouble to correct them. It is the purpose of this paper to revert to that oft-repeated objection that an abnormal production or accumulation of acids in a cell, tissue or organ can not be a potent cause of edema because our tissues contain phosphates or other "buffer" salts which have the power of taking up considerable amounts of either acid or alkali without change in "hydrogen-ion acidity."[1] Aside from the facts often pointed out before that such buffer action is not unlimited in amount, that there is a vast difference between our constantly reiterated "acid content" of tissues and their hydrogen-ion concentration, that the physiological action of even pure acids nowhere parallels their electrolytic dissociation, and that even with extreme variations in acid content there may be little change in hydration capacity if various neutral salts are present, the data in this paper show clearly enough that *from a given low point, even in the presence of such "buffer" salts, there is a progressive increase in water absorption by various proteins with every increase in the acid or alkali content of the mixture.*

II. Experimental Methods.

Dried gelatin discs prepared in the accepted fashion[2] served as the material upon which to test out the effects of different polybasic acids and their salts. For the polybasic acids we chose phosphoric and carbonic because of their importance in the animal body, and citric because of its great role in the plant economy. From the standardized solutions of these acids and of sodium hydroxide were then made the necessary primary, binary or ternary salts, by mixing the acid and alkali together in the theoretically necessary amounts.

The figures and tables are largely self-explanatory. The changes in weight (water absorption) of the gelatin discs at the end of different periods are calculated in terms of the original dry weight of the disc taken as unity.

III. Experiments with Phosphate Mixtures.

It was necessary, first, to determine the amounts of water absorbed by gelatin in different concentration of the mono-, di-, and trisodium phosphates and to discover how long a time is necessary before this water absorption is approximately complete. The results of three such experi-

[1] See for example Max Koppel, *Deut. Arch. Klin. Med.*, 112, 594 (1913); L. J. Henderson, W. W. Palmer and L. H. Newburgh, *J. Pharm. Exp. Therap.*, 5, 449 (1914).

[2] See Martin H. Fischer, "Edema and Nephritis," 2nd Ed., 57, New York, 1915.

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ments are shown in the curves of Figs. 1, 2 and 3, as well as in Tables I, II and II, which contain the data from which the curves are drawn.

TABLE I.

Gelatin—*Monosodium phosphate.*

Dry wt. of gelatin disc	0.311	0.312	0.312	0.314	0.310
Solution	5 cc. 1 *M* NaH_2PO_4 + 95 cc. H_2O	15 cc. 1 *M* NaH_2PO_4 + 85 cc. H_2O	25 cc. 1 *M* NaH_2PO_4 + 75 cc. H_2O	50 cc. 1 *M* NaH_2PO_4 + 50 cc. H_2O	100 cc. H_2O
Hours in the solution.	Gain in parts, of one part of gelatin.				
18	7.31	7.75	7.73	7.12	7.30
24	7.71	8.25	8.16	7.55	7.60
42	8.27	9.00	8.83	8.20	8.45
48	8.50	9.20	9.12	8.38	8.90
66	8.65	9.37	9.25	8.60	9.80
89	9.03	9.87	9.73	9.00	11.91
Curve designation	I	II	III	IV	H_2O

TABLE II.

Gelatin—*Disodium Phosphate.*

Dry wt. of gelatin disc	0.317	0.317	0.319	0.319	0.315
Solution	5 cc. 1 *M* Na_2HPO_4 + 95 cc. H_2O	15 cc. 1 *M* Na_2HPO_4 + 85 cc. H_2O	25 cc. 1 *M* Na_2HPO_4 + 75 cc. H_2O	50 cc. 1 *M* Na_2HPO_4 + 50 cc. H_2O	100 cc. H_2O
Hours in the solution.	Gain in parts, of one part of gelatin.				
18	9.10	8.57	7.80	5.60	6.84
24	9.74	9.16	8.30	5.91	7.41
42	10.65	10.08	9.06	6.40	8.20
48	10.91	10.32	9.30	6.56	8.60
66	11.16	10.70	9.63	6.74	10.43
89	11.65	11.22	10.20	7.24	11.22
Curve designation	I	II	III	IV	H_2O

TABLE III.

Gelatin—*Trisodium Phosphate.*

Dry wt. of gelatin disc	0.321	0.322	0.322	0.323	0.320
Solution	5 cc. 1 *M* Na_3PO_4 + 95 cc. H_2O	15 cc. 1 *M* Na_3PO_4 + 85 cc. H_2O	25 cc. 1 *M* Na_3PO_4 + 75 cc. H_2O	50 cc. 1 *M* Na_3PO_4 + 50 cc. H_2O	100 cc. H_2O
Hours in the solution.	Gain in parts, of one part of gelatin.				
18	12.44	10.30	8.44	3.77	5.32
24	13.97	11.67	9.62	4.06	6.52
42	17.31	15.28	12.94	4.63	7.75
48	18.26	16.61	14.10	4.83	8.20
66	20.93	19.71	17.20	5.10	9.21
89	22.46	22.22	21.80	5.55	10.72
Curve designation	I	II	III	IV	H_2O

As evidenced in Fig. 1, gelatin swells little more or little less in any solution of monosodium phosphate between the concentrations of 0.05

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and 0.5 *M* than it does in pure water. Fig. 2 shows that disodium phosphate in its lower concentrations tends to increase the swelling of gelatin. A maximal swelling is observed in the *least* concentrated solution of this salt. With increasing concentration the amount of swelling decreases, so that by the time the 0.5 *M* disodium phosphate solution is reached, the swelling of the gelatin is distinctly less than in pure water. A similar rule holds for like concentrations of trisodium phosphate, as shown in Fig. 3. Gelatin swells distinctly more in low concentrations of trisodium phosphate than in water, though reverse conditions come to obtain when the concentration of the phosphate is sufficiently increased.

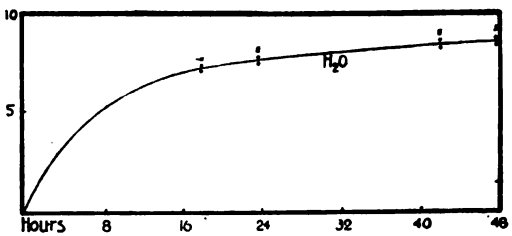

Fig. 1.

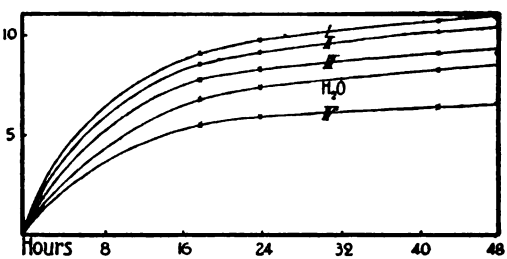

Fig. 2.

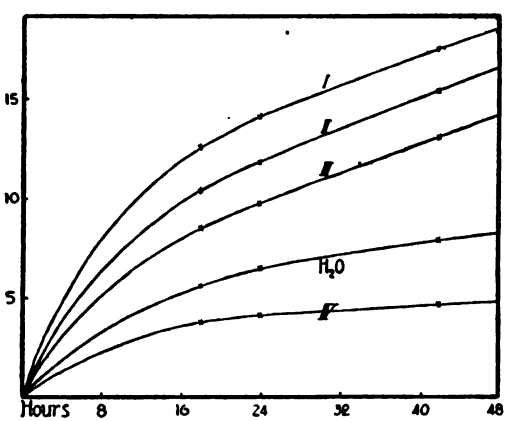

Fig. 3.

The curves of Figs. 1, 2 and 3 suffice to show that gelatin practically attains its ultimate degree of swelling in the phosphate solution at the end of 24 to 48 hours. We therefore settled upon such approximate periods for the next series of experiments in which we sought to discover the amount of swelling shown by gelatin when immersed in solutions varying from pure phosphoric acid, on the one hand, through mono-, di- and trisodium phosphate mixtures to pure sodium hydroxide on the other. It was our purpose in this experiment to see how the amount of swelling fared as more and more of the initially pure phosphoric acid was replaced by the mono-, di-, or trisodium salt. The result is shown in Table IV, and Fig. 4. The curves show the amounts of swelling at the end of 24 and of 48 hours. The low point in the curve indicative of least swelling is representative of the effects observed in the phosphate mixture numbered 6 in Table IV.

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As readily apparent, every increase in acid content to the left of this point is followed by increased swelling and the same is true for every increase in alkali content to the right of this point.

TABLE IV.

Gelatin—*Phosphoric Acid to Phosphates, to Sodium Hydroxide.*

Dry wt. of gelatin disc.....	0.363	0.366	0.367	0.368	0.368	0.368	0.368
Solution.....	10 cc. 1 *N* H_3PO_4 90 cc. H_2O	8 cc. 1 *N* H_3PO_4 + 2 cc. 1 *M* NaH_2PO_4 + 90 cc. H_2O	6 cc. 1 *N* H_3PO_4 + 4 cc. 1 *M* NaH_2PO_4 + 90 cc. H_2O	4 cc. 1 *N* H_3PO_4 + 6 cc. 1 *M* NaH_2PO_4 + 90 cc. H_2O	2 cc. 1 *N* H_3PO_4 + 8cc. 1 *M* NaH_2PO_4 + 90 cc. H_2O	10 cc. 1 *M* NaH_2PO_4 + 90 cc. H_2O	8 cc. 1 *M* NaH_2PO_4 + 2 cc. 1 *M* Na_2HPO_4 + 90 cc. H_2O
Hours in the solution.	Gain in parts, of one part of gelatin.						
24	36.51	29.14	25.60	20.21	16.24	7.42	8.21
18	44.55	35.16	29.70	24.23	19.86	8.28	9.31
Solution number	(1)	(2)	(3)	(4)	(5)	(6)	(7)
Dry wt. of gelatin disc.....	0.369	0.371	0.371	0.377	0.382	0.383	0.383
Solution.....	6 cc. 1 *M* NaH_2PO_4 + 4 cc. 1 *M* Na_2HPO_4 + 90 cc. H_2O	4 cc. 1 *M* NaH_2PO_4 + 6 cc. 1 *M* Na_2HPO_4 + 90 cc. H_2O	2 cc. 1 *M* NaH_2PO_4 + 8 cc. 1 *M* Na_2HPO_4 + 90 cc. H_2O	10 cc. 1 *M* Na_2HPO_4 + 90 cc. H_2O	8 cc. 1 *M* Na_2HPO_4 + 2 cc. 1 *M* Na_3PO_4 + 90 cc. H_2O	6 cc. 1 *M* Na_2HPO_4 + 4 cc. 1 *M* Na_3PO_4 + 90 cc. H_2O	4 cc. 1 *M* Na_2HPO_4 + 6 cc. 1 *M* Na_3PO_4 + 90 cc. H_2O
Hours in the solution.	Gain in parts, of one part of gelatin.						
24	8.44	8.50	8.90	8.61	9.52	10.86	10.51
18	9.49	9.56	10.05	9.85	11.04	13.09	12.63
Solution number	(8)	(9)	(10)	(11)	(12)	(13)	(14)
Dry wt. of gelatin disc.....	0.383	0.384	0.385	0.389	0.391	0.393	0.384
Solution.....	2 cc. 1 *M* Na_2HPO_4 + 8 cc. 1 *M* Na_3PO_4 + 90 cc. H_2O	10 cc. 1 *M* Na_3PO_4 + 90 cc. H_2O	8 cc. 1 *M* Na_3PO_4 + 2 cc. 1 *N* NaOH + 90 cc. H_2O	6 cc. 1 *M* Na_3PO_4 + 4 cc. 1 *N* NaOH + 90 cc. H_2O	4 cc. 1 *M* Na_3PO_4 + 6 cc. 1 *N* NaOH + 90 cc. H_2O	2 cc. 1 *M* Na_3PO_4 + 8 cc. 1 *N* NaOH + 90 cc. H_2O	100 cc. H_2O
Hours in the solution.	Gain in parts, of one part of gelatin.						
24	10.55	12.60	14.51	17.27	20.22	dis-solving	6.86
48	12.81	17.25	21.45	dis-solved	dis-solved	dis-solving	7.77
Solution number..	(15)	(16)	(17)	(18)	(19)	(20)	(H_2O)

It is an interesting fact that the hydrogen-ion concentration of Solution 6 is about that indicated by the turning point of methyl red (10^{-6} C_H). While we would not have it thought that the behavior of gelatin is at once to be paralleled with that of our body proteins, it is a fact that clinical observation indicates that urinary hydrogen-ion acidities approach an unsafe height when they begin to lie persistently above this point.[1]

[1] See Martin H. Fischer, *Trans. Assoc. Am. Phys.*, **27**, 630 (1912); "Edema and Nephritis," 2nd Ed., 635, New York, 1915.

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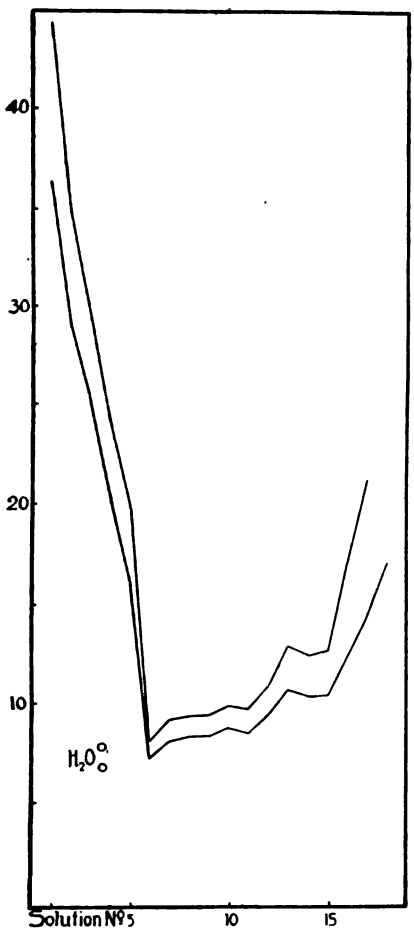

Fig. 4.

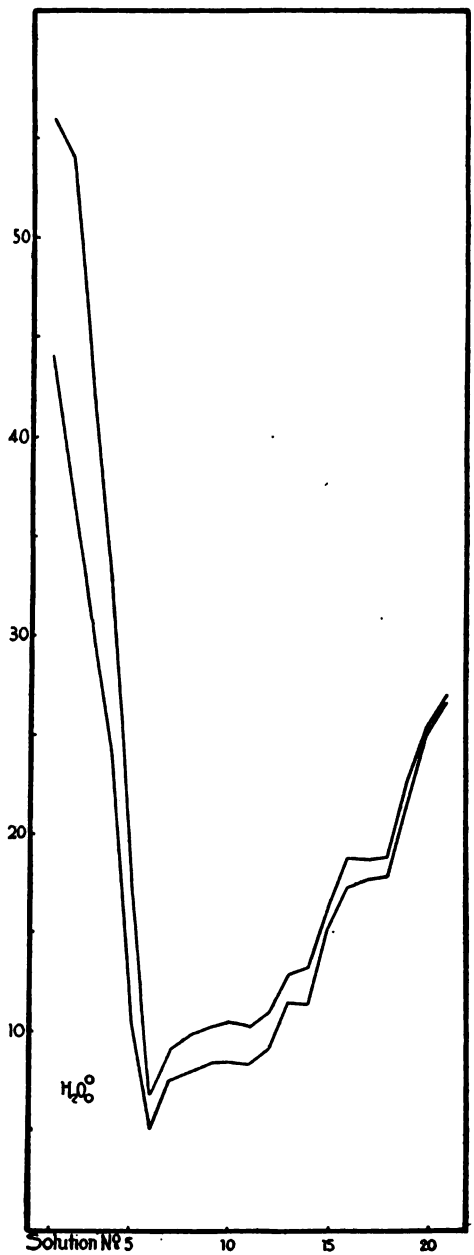

Fig. 5.

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Since the concentration of the phosphate mixtures employed in the experiments just described is relatively high (0.1 *M*), we did a second series at a concentration approximating that of the phosphates in the human body. The results are shown in Fig. 5 and Table V. The general shapes of the two curves which again represent the amounts of swelling attained in the different solutions at the ends of 18 and 42 hours are identical with those shown in Fig. 4. It is of interest to point out that the low point in the swelling curves representative of the effects of this more dilute phosphate mixture falls *below* the amount of swelling attained in pure water. There is, however, a proportionally greater swelling as we

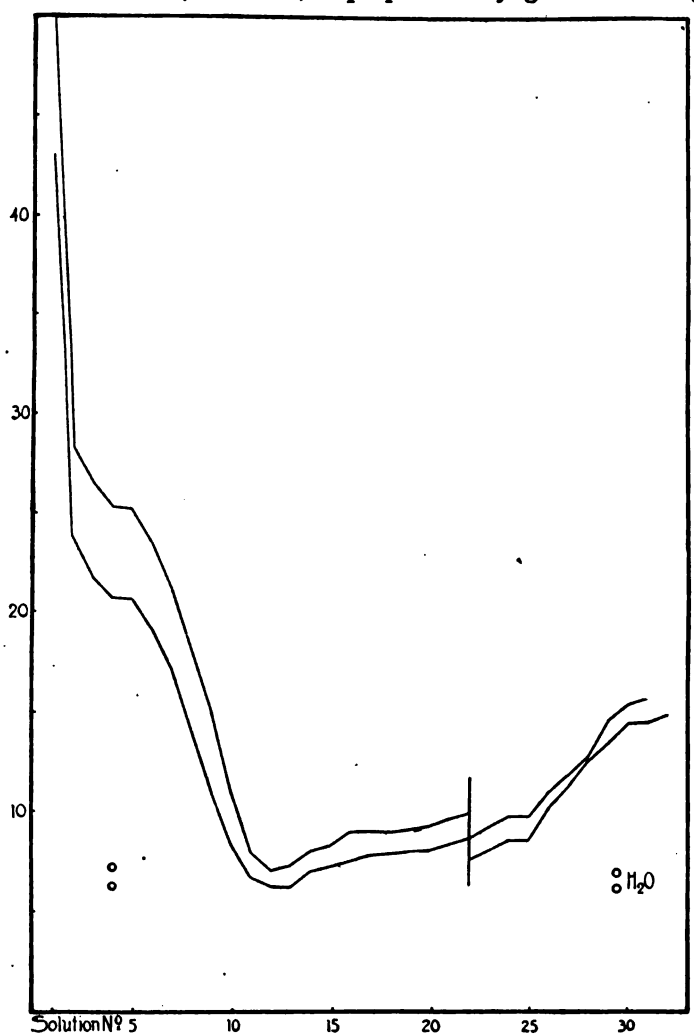

Fig. 6.

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move from this minimal point either in the direction of an increased acid or increased alkali content of the solutions, even though the proportions in the various mixtures are identical with those used in the experiments of Table IV. The absolute amounts of swelling in the acid and alkaline extremes of these more dilute phosphate mixtures are distinctly higher than in the more concentrated phosphate series previously described.

In the experiments listed in Tables IV and V, the molar concentration of the phosphate is the same throughout. While the curves of Figs. 4 and 5 show that every increase in the acid or alkali content of the phosphate mixture on either side of a low point is followed by an increased water absorption on the part of the immersed protein, it might be argued that such conditions do not obtain in the living organism where, it might be insisted, we begin with a definite concentration of a certain phosphate and then see an acid or an alkali added to this. That under such circumstances we also get a progressive increase in swelling as either the acid or alkali content of the mixture rises is shown in Figs. 6 and 7 and Tables VI and VII. The first of these figures and tables begins with a fixed concentration of disodium phosphate (0.01 *M*), the second, with the same concentration of the monosodium salt.

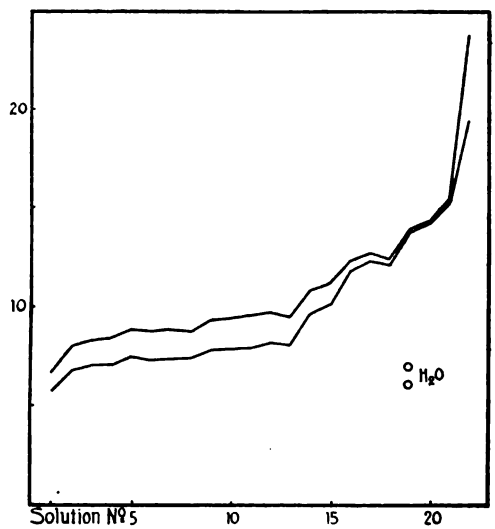

Fig. 7.

TABLE V.

Gelatin—*Phosphoric Acid to Phosphates, to Sodium Hydroxide.*

Dry wt. of gelatin disc....	0.401	0.402	0.403	0.404	0.406	0.409	0.409
Solution.....	1 cc. 1 *N* H_3PO_4 + 99 cc. H_2O	0.8 cc. 1 *N* H_3PO_4 + 0.2 cc. 1 *M* NaH_2PO_4 + 99 cc. H_2O	0.6 cc. 1 *N* H_3PO_4 + 0.4 cc. 1 *M* NaH_2PO_4 + 99 cc. H_2O	0.4 cc. 1 *N* H_3PO_4 + 0.6 cc. 1 *M* NaH_2PO_4 + 99 cc. H_2O	0.2 cc. 1 *N* H_3PO_4 + 0.8 cc. 1 *M* NaH_2PO_4 + 99 cc. H_2O	1 cc. 1 *M* NaH_2PO_4 + 99 cc. H_2O	0.8 cc. 1 *M* NaH_2PO_4 + 0.2 cc. 1 *M* Na_2HPO_4 + 99 cc. H_2O
Hours in the solution.	Gains in parts, of one part of gelatin.						
18	44.00	37.60	31.02	22.94	10.49	5.15	7.65
42	55.97	53.97	42.84	32.73	17.54	6.88	9.14
Solution number	(1)	(2)	(3)	(4)	(5)	(6)	(7)

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TABLE V (*continued*).

Dry wt. of gelatin disc.....	0.409	0.409	0.411	0.414	0.414	0.414	0.417
Solution.....	0.6 cc. 1 *M* NaH_2PO_4 + 0.4 cc. 1 *M* Na_2HPO_4 + 99 cc. H_2O	0.4 cc. 1 *M* NaH_2PO_4 + 0.6 cc. 1 *M* Na_2HPO_4 + 99 cc. H_2O	0.2 cc. 1 *M* NaH_2PO_4 + 0.8 cc. 1 *M* Na_2HPO_4 + 99 cc. H_2O	1 cc. 1 *M* Na_2HPO_4 + 99 cc. H_2O	0.8 cc. 1 *M* Na_2HPO_4 + 0.2 cc. 1 *M* Na_3PO_4 + 99 cc. H_2O	0.6 cc. 1 *M* Na_2HPO_4 + 0.4 cc. 1 *M* Na_3PO_4 + 99 cc. H_2O	0.4 cc. 1 *M* Na_2HPO_4 + 0.6 cc. 1 *M* Na_3PO_4 + 99 cc. H_2O
Hours in the solution.	Gain in parts, of one part of gelatin.						
18	8.00	8.42	8.55	8.48	9.20	11.64	11.42
42	9.80	10.24	10.50	10.31	10.98	12.90	13.26
Solution number	(8)	(9)	(10)	(11)	(12)	(13)	(14)

Dry wt. of gelatin disc....	0.419	0.420	0.421	0.424	0.425	0.425	0.426	0.408
Solution.....	0.2 cc. 1 *M* Na_2HPO_4 + 0.8 cc. 1 *M* Na_3PO_4 + 99 cc. H_2O	1 cc. 1 *M* Na_3PO_4 + 99 cc. H_2O	0.8 cc. 1 *M* Na_3PO_4 + 0.2 cc. 1 *N* NaOH + 99 cc. H_2O	0.6 cc. 1 *M* Na_3PO_4 + 0.4 cc. 1 *N* NaOH + 99 cc H_2O	0.4 cc. 1 *M* Na_3PO_4 + 0.6 cc. 1 *N* NaOH + 99 cc. H_2O	0.2 cc. 1 *M* Na_3PO_4. + 0.8 cc. 1 *N* NaOH + 99 cc. H_2O	1 cc. 1 *N* NaOH + 99 cc. H_2O	100 cc. H_2O
Hours in the solution.	Gain in parts, of one part of gelatin.							
18	15.20	17.37	17.72	17.88	21.57	25.08	26.65	6.09
42	16.44	18.77	18.74	18.84	21.74	25.43	27.06	7.50
Solution number	(15)	(16)	(17)	(18)	(19)	(20)	(21)	(H_2O)

TABLE VI.

Gelatin—*Disodium Phosphate* + *Phosphoric Acid or Sodium Hydroxide.*

Dry wt. of gelatin dics....	0.443	0.441	0.438	0.437	0.436	0.434	0.434	0.434	0.433	0.433
Solution...	100 cc. H_2O.	2 cc. 1 *N* H_3PO_4 + 98 cc. H_2O	4 cc. 0.25 *M* Na_2HPO_4 + 2.0 cc. 1 *N* H_3PO_4 94 cc. H_2O	4 cc. 0.25 *M* Na_2HPO_4 + 1.9 cc. 1 *N* H_3PO_4 94.1 cc. H_2O	4 cc. 0.25 *M* Na_2HPO_4 + 1.8 cc. 1 *N* H_3PO_4 94.2 cc. H_2O	4 cc. 0.25 *M* Na_2HPO_4 + 1.7 cc. 1 *N* H_3PO_4 94.3 cc. H_2O	4 cc. 0.25 *M* Na_2HPO_4 + 1.6 cc. 1 *N* H_3PO_4 94.4 cc. H_2O	4 cc. 0.25 *M* Na_2HPO_4 + 1.5 cc. 1 *N* H_3PO_4 94.5 cc. H_2O	4 cc. 0.25 *M* Na_2HPO_4 + 1.4 cc. 1 *N* H_3PO_4 94.6 cc. H_2O	4 cc. 0.25 *M* Na_2HPO_4 + 1.3 cc. 1 *N* H_3PO_4 94.7 cc. H_2O
Hours in the solution.	Gain in parts, of one part of gelatin.									
22	6.28	43.00	23.70	21.70	20.73	20.80	19.14	17.11	14.23	11.00
45	7.20	50.40	28.34	26.50	25.36	25.25	23.47	21.17	19.00	15.00
Solution No.	(H_2O)	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)

Dry wt. of gelatin disc....	0.431	0.431	0.423	0.422	0.421	0.420	0.419	0.419	0.416
Solution...	4 cc. 0.25 *M* Na_2HPO_4 + 1.2 cc. 1 *N* H_3PO_4 94.8 cc. H_2O	4 cc. 0.25 *M* Na_2HPO_4 + 1.1 cc. 1 *N* H_3PO_4 94.9 cc. H_2O	4 cc. 0.25 *M* Na_2HPO_4 + 1.0 cc. 1 *N* H_3PO_4 95 cc. H_2O	4 cc. 0.25 *M* Na_2HPO_4 + 0.9 cc. 1 *N* H_3PO_4 95.1 cc. H_2O	4 cc. 0.25 *M* Na_2HPO_4 + 0.8 cc. 1 *N* H_3PO_4 95.2 cc. H_2O	4 cc. 0.25 *M* Na_2HPO_4 + 0.7 cc. 1 *N* H_3PO_4 95.3 cc. H_2O	4 cc. 0.25 *M* Na_2HPO_4 + 0.6 cc. 1 *N* H_3PO_4 95.4 cc. H_2O	4 cc. 0.25 *M* Na_2HPO_4 + 0.5 cc. 1 *N* H_3PO_4 95.5 cc. H_2O	4 cc. 0.25 *M* Na_2HPO_4 + 0.4 cc. 1 *N* H_3PO_4 95.6 cc. H_2O
Hours in the solution.	Gain in parts, of one part of gelatin.								
22	8.47	6.70	6.28	6.22	7.00	7.33	7.50	7.80	7.90
45	11.10	8.00	7.10	7.37	8.03	8.34	9.14	9.07	9.08
Solution No.	(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)	(18)

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TABLE VI (*continued*).

Dry wt. of gelatin disc....	0.415	0.414	0.413	0.413	0.405	0.406	0.406	0.407
Solution...	4 cc. 0.25 *M* Na_2HPO_4 + 0.3 cc. 1 *N* H_3PO_4 95.7 cc. H_2O	4 cc. 0.25 *M* Na_2HPO_4 + 0.2 cc. 1 *N* H_3PO_4 95.8 cc. H_2O	4 cc. 0.25 *M* Na_2HPO_4 + 0.1 cc. 1 *N* H_3PO_4 95.9 cc. H_2O	4 cc. 0.25 *M* Na_2HPO_4 + 96 cc. H_2O	4 cc. 0.25 *M* Na_2HPO_4 + 96 cc. H_2O	4 cc. 0.25 *M* Na_2HPO_4 + 0.1 cc. 1 *N* NaOH 95.9 cc. H_2O	4 cc. 0.25 *M* Na_2HPO_4 + 0.2 cc. 1 *N* NaOH 95.8 cc. H_2O	4 cc. 0.25 *M* Na_2HPO_4 + 0.3 cc. 1 *N* NaOH 95.7 cc. H_2O
Hours in the solution.	Gain in parts, of one part of gelatin.							
22	8.00	8.16	8.45	8.68	7.63	8.03	8.57	8.60
45	9.10	9.30	9.70	10.06	8.72	9.20	9.82	9.70
Solution No.	(19)	(20)	(21)	(22)	(23)	(24)	(25)	(26)

Dry wt. of gelatin disc....	0.407	0.407	0.408	0.408	0.409	0.410	0.411	0.412
Solution...	4 cc. 0.25 *M* Na_2HPO_4 + 0.4 cc. 1 *N* NaOH 95.6 cc. H_2O	4 cc. 0.25 *M* Na_2HPO_4 + 0.5 cc. 1 *N* NaOH 95.5 cc. H_2O	4 cc. 0.25 *M* Na_2HPO_4 + 0.6 cc. 1 *N* NaOH 95.4 cc. H_2O	4 cc. 0.25 *M* Na_2HPO_4 + 0.7 cc. 1 *N* NaOH 95.3 cc. H_2O	4 cc. 0.25 *M* Na_2HPO_4 + 0.8 cc. 1 *N* NaOH 95.2 cc. H_2O	4 cc. 0.25 *M* Na_2HPO_4 + 0.9 cc. 1 *N* NaOH 95.1 cc. H_2O	4 cc. 0.25 *M* Na_2HPO_4 + 1.0 cc. 1 *N* NaOH 95 cc. H_2O	100 cc. H_2O
Hours in the solution.	Gain in parts, of one part of gelatin.							
22	10.29	11.21	12.65	13.41	14.40	14.57	14.87	6.04
45	11.05	11.80	12.72	13.65	15.40	15.70	14.81	6.82
Solution No.	(27)	(28)	(29)	(30)	(31)	(32)	(33)	(H_2O)

TABLE VII.

Gelatin—*Monosodium Phosphate, with Increasing Amounts of Sodium Hydroxide.*

Dry wt. of gelatin disc....	0.388	0.390	0.391	0.392	0.392	0.393	0.393	0.393
Solution.....	1 cc. 1 *M* NaH_2PO_4 +99 cc. H_2O	1 cc. 1 *M* NaH_2PO_4 +0.1 cc. 1 *N* NaOH +98.9 cc. H_2O	1 cc. 1 *M* NaH_2PO_4 +0.2 cc. 1 *N* NaOH +98.8 cc. H_2O	1 cc. 1 *M* NaH_2PO_4 +0.3 cc. 1 *N* NaOH +98.7 cc. H_2O	1 cc. 1 *M* NaH_2PO_4 +0.4 cc. 1 *N* NaOH +98.6 cc. H_2O	1 cc. 1 *M* NaH_2PO_4 +0.5 cc. 1 *N* NaOH +98.5 cc. H_2O	1 cc. 1 *M* NaH_2PO_4 +0.6 cc. 1 *N* NaOH +98.4 cc. H_2O	1 cc. 1 *M* NaH_2PO_4 +0.7 cc. 1 *N* NaOH +98.3 cc. H_2O
Hours in the solution.	Gain in parts, of one part of gelatin.							
20	5.90	6.90	7.11	7.11	7.65	7.47	7.50	7.53
44	6.78	8.10	8.44	8.56	9.00	8.80	9.00	8.83
Solution No...	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)

Dry wt. of gelatin disc....	0.394	0.395	0.395	0.397	0.398	0.400	0.400
Solution.....	1 cc. 1 *M* NaH_2PO_4 + 0.8 cc. 1 *N* NaOH + 98.2 cc. H_2O	1 cc. 1 *M* NaH_2PO_4 + 0.9 cc. 1 *N* NaOH + 98.1 cc. H_2O	1 cc. 1 *M* NaH_2PO_4 + 1.0 cc. 1 *N* NaOH + 98 cc. H_2O	1 cc. 1 *M* NaH_2PO_4 + 1.1 cc. 1 *N* NaOH + 97.9 cc. H_2O	1 cc. 1 *M* NaH_2PO_4 + 1.2 cc. 1 *N* NaOH + 97.8 cc. H_2O	1 cc. 1 *M* NaH_2PO_4 + 1.3 cc. 1 *N* NaOH + 97.7 cc. H_2O	1 cc. 1 *M* NaH_2PO_4 + 1.4 cc. 1 *N* NaOH + 97.6 cc. H_2O
Hours in the solution.	Gain in parts, of one part of gelatin.						
20	8.02	8.12	8.17	8.37	8.20	9.80	10.25
44	9.45	9.57	9.70	9.84	9.60	11.03	11.30
Solution No...	(9)	(10)	(11)	(12)	(13)	(14)	(15)

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TABLE VII (*continued*).

Dry wt. of gelatin disc....	0.401	0.403	0.403	0.403	0.404	0.405	0.405	0.405
Solution.....	1 cc. 1 *M* NaH_2PO_4 + 1.5 cc. 1 *N* NaOH + 97.5 cc. H_2O	1 cc. 1 *M* NaH_2PO_4 + 1.6 cc. 1 *N* NaOH + 97.4 cc. H_2O	1 cc. 1 *M* NaH_2PO_4 + 1.7 cc. 1 *N* NaOH + 97.3 cc. H_2O	1 cc. 1 *M* NaH_2PO_4 + 1.8 cc. 1 *N* NaOH + 97.2 cc. H_2O	1 cc. 1 *M* NaH_2PO_4 + 1.9 cc. 1 *N* NaOH + 97.1 cc. H_2O	1 cc. 1 *M* NaH_2PO_4 + 2.0 cc. 1 *N* NaOH + 97 cc. H_2O	+ 2.0 cc. 1 *N* NaOH + 98 cc. H_2O	100 cc. H_2O
Hours in the solution.	Gain in parts, of one part of gelatin.							
20	12.00	12.51	12.28	14.04	14.42	15.55	19.65	6.13
44	12.54	12.94	12.56	14.10	14.47	15.42	23.91	7.06
Solution No..	(16)	(17)	(18)	(19)	(20)	(21)	(22)	(H_2O)

A set of experiments was next made by beginning with a fixed concentration of acid (0.03 *N*) and adding to this progressively greater amounts of alkali. Under such circumstances there are seen, of course, the double effects of decrease in concentration of free acid with increase in amount of phosphate present. The general shape of the water absorption curve as shown in Fig. 8 and Table VIII is, however, that familiar to us from the previous experiments. A low point is again found in the middle of the curve when one-third of the replaceable hydrogen of the phosphoric acid has been neutralized by alkali, in other words, when we deal with a solution which is practically pure monosodium phosphate. Addition of more alkali leads to increased swelling up to the high point at the right of the curve which represents the theoretically pure solution of trisodium phosphate.

TABLE VIII.

Gelatin—*Phosphoric Acid with Increasing Amounts of Sodium Hydroxide.*

Dry wt. of gelatin disc....	0.343	0.343	0.345	0.347	0.360	0.363	0.365	0.367
Solution.....	3 cc. 1 *N* H_3PO_4 + 97 cc. H_2O	3 cc. 1 *N* H_3PO_4 + 0.1 cc. 1 *N* NaOH + 96.9 cc. H_2O	3 cc. 1 *N* H_3PO_4 + 0.2 cc. 1 *N* NaOH + 96.8 cc. H_2O	3 cc. 1 *N* H_3PO_4 + 0.3 cc. 1 *N* NaOH + 96.7 cc. H_2O	3 cc. 1 *N* H_3PO_4 + 0.4 cc. 1 *N* NaOH + 96.6 cc. H_2O	3 cc. 1 *N* H_3PO_4 + 0.5 cc. 1 *N* NaOH + 96.5 cc. H_2O	3 cc. 1 *N* H_3PO_4 + 0.6 cc. 1 *N* NaOH + 96.4 cc. H_2O	3 cc. 1 *N* H_3PO_4 + 0.7 cc. 1 *N* NaOH + 96.3 cc. H_2O
Hours in the solution.	Gain in parts, of one part of gelatin.							
20	69.32	62.85	58.65	58.45	46.60	43.00	31.00	22.31
44	84.68	75.11	70.60	69.90	58.17	54.16	42.20	33.87
Solution No...	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)

Dry wt. of gelatin disc....	0.367	0.367	0.367	0.370	0.370	0.370	0.371	0.374
Solution.....	3 cc. 1 *N* H_3PO_4 + 0.8 cc. 1 *N* NaOH + 96.2 cc. H_2O	3 cc. 1 *N* H_3PO_4 + 0.9 cc. 1 *N* NaOH + 96.1 cc. H_2O	3 cc. 1 *N* H_3PO_4 + 1.0 cc. 1 *N* NaOH + 96.0 cc. H_2O	3 cc. 1 *N* H_3PO_4 + 1.1 cc. 1 *N* NaOH + 95.9 cc. H_2O	3 cc. 1 *N* H_3PO_4 + 1.2 cc. 1 *N* NaOH + 95.8 cc. H_2O	3 cc. 1 *N* H_3PO_4 + 1.3 cc. 1 *N* NaOH + 95.7 cc. H_2O	3 cc. 1 *N* H_3PO_4 + 1.4 cc. 1 *N* NaOH + 95.6 cc. H_2O	3 cc. 1 *N* H_3PO_4 + 1.5 cc. 1 *N* NaOH + 95.5 cc. H_2O
Hours in the solution.	Gain in parts, of one part of gelatin.							
20	15.30	8.31	7.10	8.03	8.68	8.74	9.35	9.60
44	24.32	11.28	8.27	9.41	10.27	10.44	11.16	11.56
Solution No...	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)

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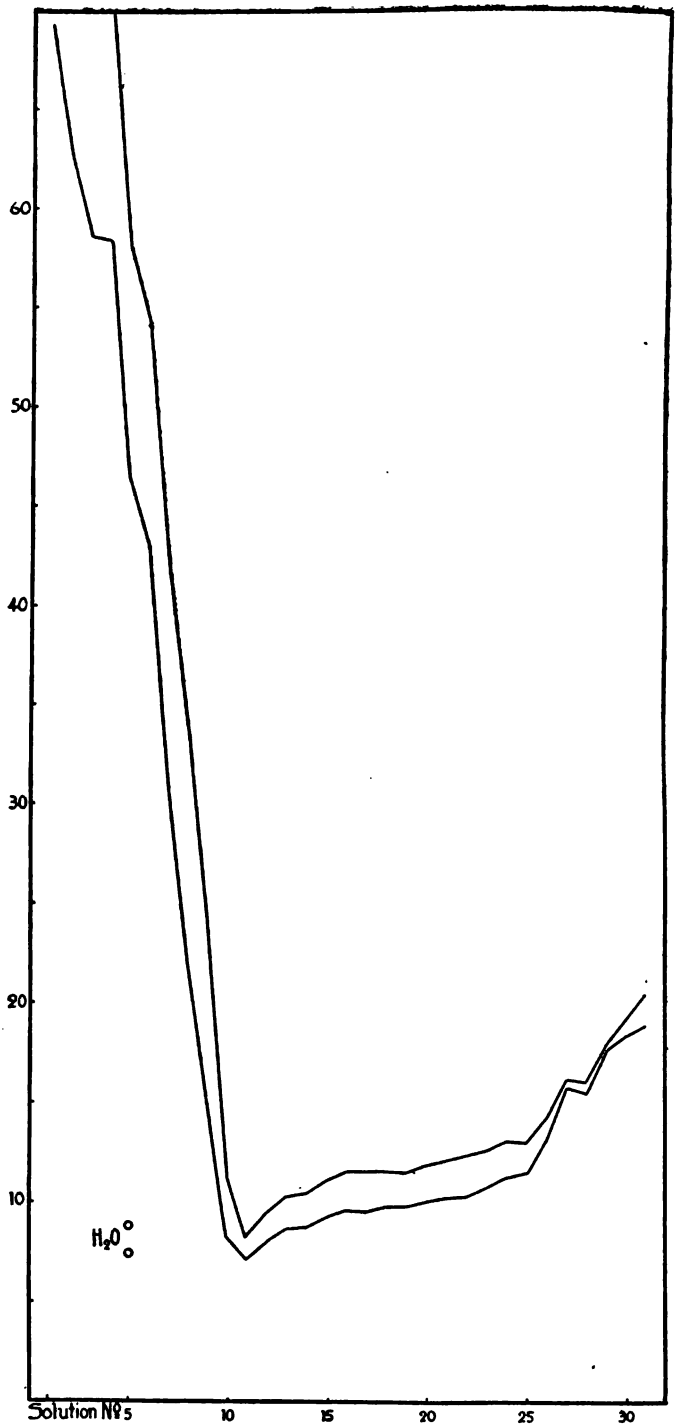

Fig. 8.

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TABLE VIII (*continued*).

Dry wt. of gelatin disc....	0.380	0.382	0.383	0.384	0.386	0.385	0.388	0.388
Solution.....	3 cc. 1 *N* H_3PO_4 + 1.6 cc. 1 *N* NaOH + 95.4 cc. H_2O	3 cc. 1 *N* H_3PO_4 + 1.7 cc. 1 *N* NaOH + 95.3 cc. H_2O	3 cc. 1 *N* H_3PO_4 + 1.8 cc. 1 *N* NaOH + 95.2 cc. H_2O	3 cc. 1 *N* H_3PO_4 + 1.9 cc. 1 *N* NaOH + 95.1 cc. H_2O	3 cc. 1 *N* H_3PO_4 + 2.0 cc. 1 *N* NaOH + 95.0 cc. H_2O	3 cc. 1 *N* H_3PO_4 + 2.1 cc. 1 *N* NaOH + 94.9 cc. H_2O	3 cc. 1 N H_3PO_4 + 2.2 cc. 1 *N* NaOH + 94.8 cc. H_2O	3 cc. 1 *N* H_3PO_4 + 2.3 cc. 1 *N* NaOH + 94.7 cc. H_2O
Hours in the solution.	Gain in parts, of one part of gelatin.							
20	9.49	9.81	9.81	10.00	10.23	10.26	10.80	11.28
44	11.31	11.60	11.57	11.90	12.14	12.40	12.61	13.12
Solution No...	(17)	(18)	(19)	(20)	(21)	(22)	(23)	(24)

Dry wt. in gelatin.....	0.388	0.388	0.389	0.391	0.391	0.392	0.394	0.394
Solution.....	3 cc. 1 *N* H_3PO_4 + 2.4 cc. 1 *N* NaOH + 94.6 cc. H_2O	3 cc. 1 *N* H_3PO_4 + 2.5 cc. 1 *N* NaOH + 94.5 cc. H_2O	3 cc. 1 *N* H_3PO_4 + 2.6 cc. 1 *N* NaOH + 94.4 cc. H_2O	3 cc. 1 *N* H_3PO_4 + 2.7 cc. 1 *N* NaOH + 94.3 cc. H_2O	3 cc. 1 *N* H_3PO_4 + 2.8 cc. 1 *N* NaOH + 94.2 cc. H_2O	3 cc. 1 *N* H_3PO_4 + 2.9 cc. 1 *N* NaOH + 94.1 cc. H_2O	3 cc. 1 *N* H_3PO_4 + 3.0 cc. 1 *N* NaOH + 94 cc. H_2O	100 cc. H_2O
Hours in the solution.	Gain in parts, of one part of gelatin.							
20	11.52	13.14	15.81	15.57	17.71	19.40	19.91	7.45
44	13.00	14.24	16.25	16.17	18.03	19.37	20.50	8.80
Solution No...	(25)	(26)	(27)	(28)	(29)	(30)	(31)	(H_2O)

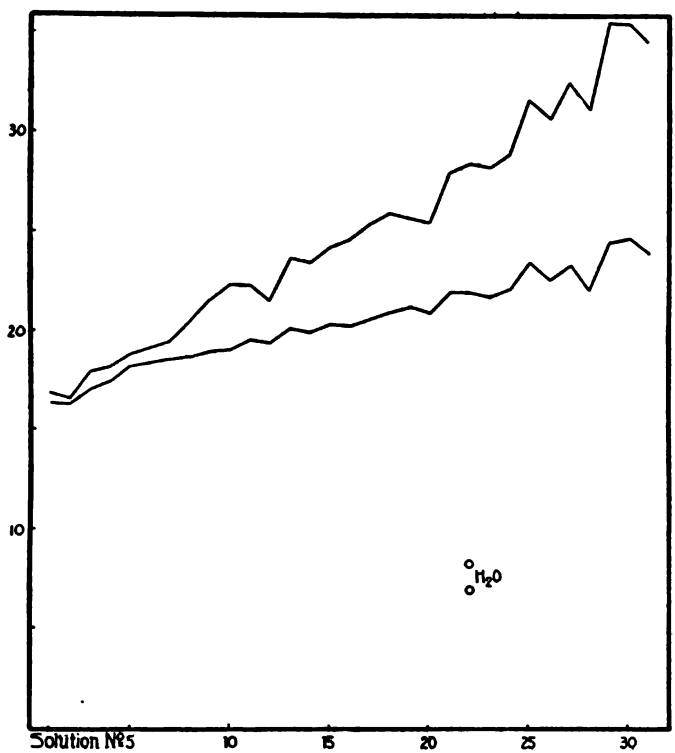

Fig. 9.

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A final series of phosphate experiments is shown in Fig. 9 and Table IX. Here a fixed amount of alkali (0.03 *N*) was neutralized by adding gradually increasing amounts of phosphoric acid. There are shown, in other words, the effects of simultaneous reduction of acid with increase in amount of phosphate present. The water absorption curve falls as the neutralization progresses, until a low point is attained in the theoretically pure solution of trisodium phosphate.

TABLE IX.

Gelatin—*Sodium Hydroxide with Decreasing Amounts of Phosphoric Acid.*

Dry wt. of gelatin discs...	0.347	0.346	0.343	0.342	0.341	0.341	0.340	0.340
Solution.....	3 cc. 1 *N* NaOH +3.0 cc. 1 *N* H_3PO_4 +94 cc. H_2O	3 cc. 1 *N* NaOH +2.9 cc. 1 *N* H_3PO_4 +94.1 cc. H_2O	3 cc. 1 *N* NaOH +2.8 cc. 1 *N* H_3PO_4 +94.2 cc. H_2O	3 cc. 1 *N* NaOH +2.7 cc. 1 *N* H_3PO_4 +94.3 cc. H_2O	3 cc. 1 *N* NaOH +2.6 cc. 1 *N* H_3PO_4 +94.4 cc. H_2O	3 cc. 1 *N* NaOH +2.5 cc. 1 *N* H_3PO_4 +94.5 cc. H_2O	3 cc. 1 *N* NaOH +2.4 cc. 1 *N* H_3PO_4 +94.6 cc. H_2O	3 cc. 1 *N* NaOH +2.3 cc. 1 *N* H_3PO_4 +94.7 cc. H_2O
Hours in the solution.	Gain in parts, of one part of gelatin.							
20	16.46	16.40	17.17	17.55	18.32	18.36	18.70	18.85
44	17.00	16.69	18.02	18.30	18.82	18.80	19.53	20.53
Solution No...	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
Dry wt. of gelatin discs...	0.340	0.339	0.338	0.338	0.338	0.338	0.337	0.336
Solution.....	3 cc. 1 *N* NaOH +2.2 cc. 1 *N* H_3PO_4 +94.8 cc. H_2O	3 cc. 1 *N* NaOH +2.1 cc. 1 *N* H_3PO_4 +94.9 cc. H_2O	3 cc. 1 *N* NaOH +2.0 cc. 1 *N* H_3PO_4 +95 cc. H_2O	3 cc. 1 *N* NaOH +1.9 cc. 1 N H_3PO_4 +95.1 cc. H_2O	3 cc. 1 *N* NaOH +1.8 cc. 1 *N* H_3PO_4 +95.2 cc. H_2O	3 cc. 1 *N* NaOH +1.7 cc. 1 *N* H_3PO_4 +95.3 cc. H_2O	3 cc. 1 *N* NaOH +1.6 cc. 1 *N* H_3PO_4 +95.4 cc. H_2O	3 cc. 1 *N* NaOH +1.5 cc. 1 *N* H_3PO_4 +95.5 cc. H_2O
Hours in the solution.	Gain in parts, of one part of gelatin.							
20	19.00	19.15	19.65	19.47	20.25	20.03	20.45	20.35
44	21.60	22.42	22.43	21.65	23.76	23.55	24.37	24.70
Solution No...	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)
Dry wt. of gelatin discs...	0.336	0.336	0.335	0.335	0.334	0.332	0.331	0.331
Solution.....	3 cc. 1 *N* NaOH +1.4 cc. 1 *N* H_3PO_4 +95.6 cc. H_2O	3 cc. 1 *N* NaOH +1.3 cc. 1 *N* H_3PO_4 +95.7 cc. H_2O	3 cc. 1 *N* NaOH +1.2 cc. 1 *N* H_3PO_4 +95.8 cc. H_2O	3 cc. 1 *N* NaOH +1.1 cc. 1 *N* H_3PO_4 +95.9 cc. H_2O	3 cc. 1 *N* NaOH +1.0 cc. 1 *N* H_3PO_4 +96 cc. H_2O	3 cc. 1 *N* NaOH +0.9 cc. 1 *N* H_3PO_4 +96.1 cc. H_2O	3 cc. 1 *N* NaOH +0.8 cc. 1 *N* H_3PO_4 +96.2 cc. H_2O	3 cc. 1 *N* NaOH +0.7 cc. 1 *N* H_3PO_4 +96.3 cc. H_2O
Hours in the solution.	Gain in parts, of one part of gelatin.							
20	20.77	21.05	21.30	20.97	22.06	22.04	21.85	22.21
44	25.55	26.00	25.85	25.58	28.14	28.50	28.31	29.03
Solution No...	(17)	(18)	(19)	(20)	(21)	(22)	(23)	(24)
Dry wt. of gelatin discs...	0.330	0.330	0.330	0.329	0.329	0.328	0.327	0.347
Solution.....	3 cc. 1 *N* NaOH +0.6 cc. 1 *N* H_3PO_4 +96.4 cc. H_2O	3 cc. 1 *N* NaOH +0.5 cc. 1 *N*. H_3PO_4 +96.5 cc. H_2O	3 cc. 1 *N* NaOH +0.4 cc. 1 *N* H_3PO_4 +96.6 cc. H_2O	3 cc. 1 N NaOH +0.3 cc. 1 *N* H_3PO_4 +96.7 cc. H_2O	3 cc. 1 *N* NaOH +0.2 cc. 1 *N* H_3PO_4 +96.8 cc. H_2O	3 cc. 1 *N* NaOH +0.1 cc. 1 *N* H_3PO_4 +96.9 cc. H_2O	3 cc. 1 *N* NaOH +97 cc. H_2O	100 cc. H_2O
Hours in the solution.	Gain in parts, of one part of gelatin.							
20	23.56	22.70	23.48	22.13	24.51	24.73	24.00	6.94
44	31.80	30.81	32.66	31.26	35.68	35.61	34.64	8.33
Solution No...	(25)	(26)	(27)	(28)	(29)	(30)	(31)	(H_2O)

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IV. Experiments with Citrate Mixtures.

We studied next the effects of citric acid and the citrates upon the swelling of gelatin. The citrate solutions were prepared by adding to each other the theoretically necessary amounts of carefully standardized citric acid and sodium hydroxide solutions.

In Figs. 10, 11 and 12, which portray graphically the experimental findings contained in Tables X, XI and XII, are shown the effects, respectively, of mono-, di-, and trisodium citrate in different concentrations upon the swelling of gelatin. As evident in Fig. 10, monosodium citrate in all the concentrations used increases the amount of water absorbed by gelatin over and above the amount absorbed in pure water. The same is true of the lower concentrations of equimolar solutions of disodium citrate. For both of these salts there is a progressive decrease in swelling with increase in the concentration of the salt. As evident in the lowermost curve of Fig. 11, a sufficiently high concentration of disodium citrate makes gelatin swell even less than in pure water. The effects of trisodium citrate are shown in Fig. 12. Low concentrations of this salt also increase the amount of water absorption over the amount absorbed in pure water, but with increasing concentration there is less and less swelling, until the amounts of water absorbed in the higher concentrations of the trisodium citrate are distinctly less than in pure water.

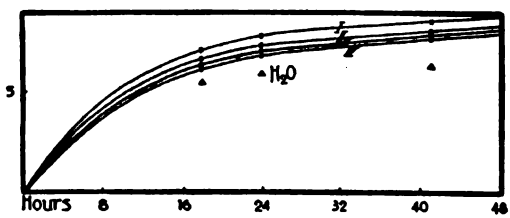

Fig. 10.

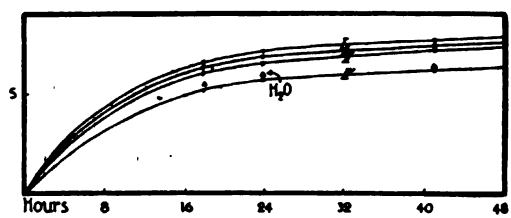

Fig. 11.

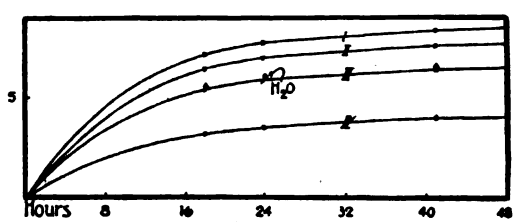

Fig. 12.

Having determined in this fashion the effects of different concentrations of the different citrates, we investigated the swelling of gelatin in citrate mixtures varying from the extreme on the one side of pure citric acid through equimolar concentrations of mono-, di- and trisodium citrate to pure sodium hydroxide upon the other. The results as shown in Fig. 13 and Table XIII are self-explanatory. The three curves show the amounts of water absorbed at the end of 24, 48 and 72 hours. As

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TABLE X.

Gelatin—*Monosodium Citrate.*

Dry wt. of gelatin discs.....	0.370	0.373	0.373	0.373	0.370
Solution.....	5 cc. 1 *M* monosod. citrate + 95 cc. H_2O	15 cc. 1 *M* monosod. citrate + 85 cc. H_2O	25 cc. 1 *M* monosod. citrate + 75 cc. H_2O	50 cc. 1 *M* monosod. citrate + 50 cc. H_2O	100 cc. H_2O
Hours in the solution.	Gain in parts, of one part of gelatin.				
18	7.17	6.74	6.20	6.23	5.52
24	7.91	7.47	7.11	7.12	5.94
41	8.69	8.16	8.27	8.01	6.35
48	8.92	8.44	8.59	8.40	6.52
66	9.30	8.81	9.08	9.00	6.84
71	9.35	8.85	9.12	9.11	6.90
91	9.51	8.88	9.41	9.28	7.27
Curve designation	(I)	(II)	(III)	(IV)	(H_2O)

TABLE XI.

Gelatin—*Disodium Citrate.*

Dry wt. of gelatin discs.....	0.365	0.367	0.369	0.369	0.365
Solution.....	5 cc. 1 *M* disod. citrate + 95 cc. H_2O	15 cc. 1 *M* disod. citrate + 85 cc. H_2O	25 cc. 1 *M* disod. citrate + 75 cc. H_2O	50 cc. 1 *M* disod. citrate + 50 cc. H_2O	100 cc. H_2O
Hours in the solution.	Gain in parts, of one part of gelatin.				
18	6.39	6.38	5.11	5.12	5.47
24	6.88	6.92	6.44	5.78	5.92
41	7.34	7.41	7.26	6.24	6.31
48	7.77	7.58	7.49	6.48	6.49
66	7.70	7.83	7.74	6.74	6.89
71	7.76	7.84	7.71	6.77	6.96
91	7.82	7.95	7.89	7.86	7.37
Curve designation	(I)	(II)	(III)	(IV)	(H_2O)

TABLE XII.

Gelatin—*Trisodium Citrate.*

Dry wt. of gelatin discs.....	0.363	0.363	0.363	0.364	0.363
Solution.....	5 cc. 1 *M* trisod. citrate + 95 cc. H_2O	15 cc. 1 *M* trisod. citrate + 85 cc. H_2O	25 cc. 1 *M* trisod. citrate + 75 cc. H_2O	50 cc. 1 *M* trisod. citrate + 50 cc. H_2O	100 cc. H_2O
Hours in the solution.	Gain in parts, of one part of gelatin.				
18	7.12	6.42	5.51	3.12	5.53
24	7.75	7.01	6.04	3.52	5.98
41	8.23	7.51	6.51	3.90	6.35
48	8.50	7.69	6.68	4.02	6.58
66	8.73	7.95	6.93	4.21	6.99
71	8.73	7.96	6.96	4.23	7.08
91	8.81	8.06	7.04	4.30	7.62
Curve designation.....	(I)	(II)	(III)	(IV)	(H_2O)

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readily evident, most swelling occurs in the pure citric acid, and less and less swelling as the pure citric acid gives way to the monosodium citrate.

TABLE XIII.

Gelatin—*Citric Acid, to Citrates, to Sodium Hydroxide.*

Dry wt. of gelatin discs...	0.332	0.334	0.335	0.335	0.336	0.338	0.339
Solution.....	10 cc. 1 *N* citric acid +90 cc. H_2O	8 cc. 1 *N* citric acid +2 cc. 1 *M* monosod. citrate +90 cc. H_2O	6 cc. 1 *N* citric acid +4 cc. 1 *M* monosod. citrate +90 cc. H_2O	4 cc. 1 *N* citric acid +6 cc. 1 *M* monosod. citrate +90 cc. H_2O	2 cc. 1 *N* citric acid +8 cc. 1 *M* monosod. citrate +90 cc. H_2O	10 cc. 1 *M* monosod. citrate +90 cc. H_2O	8 cc. 1 *M* monosod. citrate +2 cc. 1 *M* disod. citrate +90 cc. H_2O
Hours in the solution.	Gain in parts, of one part of gelatin.						
24	46.10	27.58	18.29	14.11	11.08	9.02	7.66
48	51.08	33.14	22.71	17.04	13.09	10.40	8.84
72	60.70	36.72	25.10	18.53	14.18	11.16	9.47
Solution No....	(1)	(2)	(3)	(4)	(5)	(6)	(7)

Dry wt. of gelatin discs...	0.340	0.341	0.341	0.342	0.342	0.345	0.345
Solution.....	6 cc. 1 *M* monosod. citrate +4 cc. 1 *M* disod. citrate +90 cc. H_2O	4 cc. 1 *M* monosod. citrate +6 cc. 1 *M* disod. citrate +90 cc. H_2O	2 cc. 1 *M* monosod. citrate +8 cc. 1 *M* disod. citrate +90 cc. H_2O	10 cc. 1 *M* disod. citrate +90 cc. H_2O	8 cc. 1 *M* disod. citrate +2 cc. 1 *M* trisod. citrate +90 cc. H_2O	6 cc. 1 *M* disod. citrate +4 cc. 1 *M* trisod. citrate +90 cc. H_2O	4 cc. 1 *M* disod. citrate +6 cc. 1 *M* trisod. citrate +90 cc. H_2O
Hours in the solution.	Gain in parts, of one part of gelatin.						
24	7.60	7.50	7.55	8.02	8.05	8.22	8.26
48	8.61	8.45	8.44	8.93	8.96	8.80	9.23
72	9.27	9.00	9.08	9.46	9.50	9.48	10.02
Solution No....	(8)	(9)	(10)	(11)	(12)	(13)	(14)

Dry wt. of gelatin discs...	0.346	0.350	0.351	0.352	0.352	0.353	0.353	0.350
Solution.....	2 cc. 1 *M* disod. citrate +8 cc. 1 *M* trisod. citrate +90 cc. H_2O	10 cc. 1 *M* trisod. citrate +90 cc. H_2O	8 cc. 1 *M* trisod. citrate +2 cc. 1 *N* NaOH +90 cc. H_2O	6 cc. 1 *M* trisod. citrate +4 cc. 1 *N* NaOH +90 cc. H_2O	4 cc. 1 *M* trisod. citrate +6 cc. 1 *N* NaOH +90 cc. H_2O	2 cc. 1 *M* trisod. citrate +8 cc. 1 *N* NaOH +90 cc. H_2O	10 cc. 1 *N* NaOH +90 cc. H_2O	100 cc. H_2O
Hours in the solution.	Gain in parts, of one part of gelatin.							
24	8.19	8.16	10.51	14.22	17.01	24.22+	dissolving	6.35
48	9.34	9.03	12.90	20.54	27.83+	dissolving	dissolved	7.12
72	9.54	9.41	15.06	28.83+	dissolving			8.11
Solution No...	(15)	(16)	(17)	(18)	(19)	(20)	(21)	(H_2O)

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Between monosodium citrate, disodium citrate and trisodium citrate there is little change in the amount of water absorbed, this portion of the curve describing a gentle arc. As the excess of alkali appears in the mixture, the curve again ascends steeply.

V. Experiments with Carbonate Mixtures.

The swelling of gelatin in carbonate mixtures has also been given some study. The results here again confirm the general conclusions as previously cited for phosphates and citrates. In the carbonate series we began with pure sodium bicarbonate and gradually replaced this by molecularly equivalent amounts of sodium carbonate, and this in turn by of sodium hydroxide. The effects upon the swelling of gelatin as we pass from the sodium bicarbonate through the sodium carbonate to sodium hydroxide is shown in Fig. 14 and Table XIV. The curves show the amounts of swelling at the end of $5^1/_2$, 29 and 53 hours. As is clearly apparent, gelatin swells more in a solution of sodium bicarbonate than in pure water and the amount of this swelling increases progressively as we pass from the sodium bicarbonate to sodium carbonate and then more abruptly as we enter the realm of the purer sodium hydroxide.

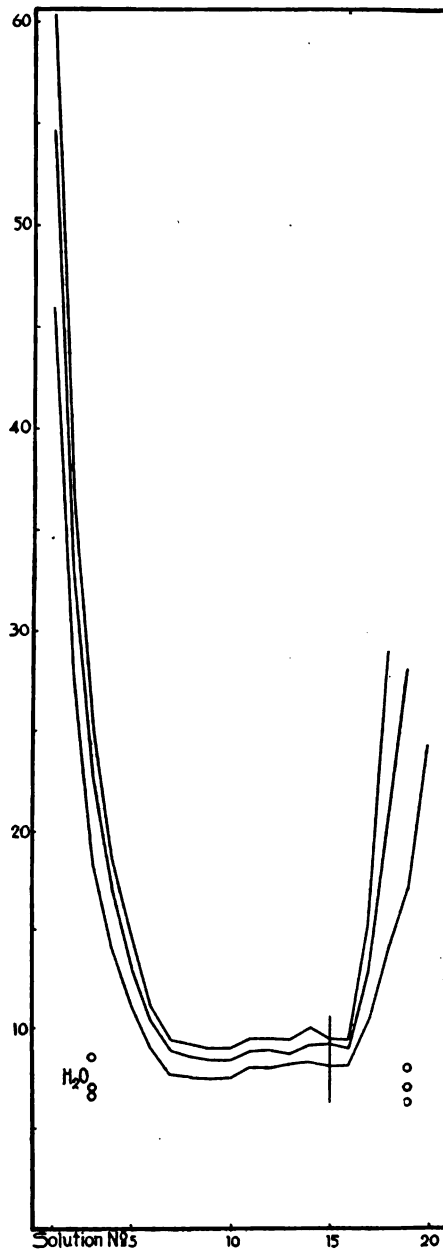

Fig. 13.

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TABLE XIV.

Gelatin—*Sodium Bicarbonate, to Sodium Carbonate, to Sodium Hydroxide.*

Dry wt. of gelatin disc....	0.368	0.369	0.370	0.370	0.371	0.371	0.372
Solution.....	2 cc. 1 *M* $NaHCO_3$ + 98 cc. H_2O	1.9 cc. 1 *M* $NaHCO_3$ + 0.1 cc. 1 *M* Na_2CO_3 + 98 cc. H_2O	1.8 cc. 1 *M* $NaHCO_3$ + 0.2 cc. 1 *M* Na_2CO_3 + 9.8 cc. H_2O	1.7 cc. 1 *M* $NaHCO_3$ + 0.3 cc. 1 *M* Na_2CO_3 + 98 cc. H_2O	1.6 cc. 1 *M* $NaHCO_3$ + 0.4 cc. 1 *M* Na_2CO_3 + 98 cc. H_2O	1.5 cc. 1 *M* $NaHCO_3$ + 0.5 cc. 1 *M* Na_2CO_3 + 98 cc. H_2O	1.4 cc. 1 *M* $NaHCO_3$ + 0.6 cc. 1 *M* Na_2CO_3 + 98 cc. H_2O
Hours in the solution.	Gain in parts, of one part of gelatin.						
5.5	5.18	5.30	5.65	6.00	5.66	5.58	5.97
29	11.52	11.84	12.07	12.56	11.91	12.00	12.35
53	13.05	13.40	13.51	14.00	13.30	13.33	13.75
Solution No...	(1)	(2)	(3)	(4)	(5)	(6)	(7)

Dry wt. of gelatin disc....	0.372	0.373	0.375	0.376	0.377	0.377	0.379
Solution.....	1.3 cc. 1 *M* $NaHCO_3$ + 0.7 cc. 1 *M* Na_2CO_3 + 98 cc. H_2O	1.2 cc. 1 *M* $NaHCO_3$ + 0.8 cc. 1 *M* Na_2CO_3 + 98 cc. H_2O	1.1 cc. 1 *M* $NaHCO_3$ + 0.9 cc. 1 *M* Na_2CO_3 + 98 cc. H_2O	1.0 cc. 1 *M* $NaHCO_3$ + 1.0 cc. 1 *M* Na_2CO_3 + 98 cc. H_2O	0.9 cc. 1 *M* $NaHCO_3$ + 1.1 cc. 1 *M* Na_2CO_3 + 98 cc. H_2O	0.8 cc. 1 *M* $NaHCO_3$ + 1.2 cc. 1 *M* Na_2CO_3 + 98 cc. H_2O	0.7 cc. 1 *M* $NaHCO_3$ + 1.3 cc. 1 *M* Na_2CO_3 + 98 cc. H_2O
Hours in the solution.	Gain in parts, of one part of gelatin.						
5.5	5.70	6.25	6.40	6.32	6.51	6.18	6.00
29	11.90	12.20	12.22	12.06	12.30	12.16	12.11
53	13.41	13.47	13.60	13.55	13.71	13.63	13.50
Solution No...	(8)	(9)	(10)	(11)	(12)	(13)	(14)

Dry wt. of gelatin disc....	0.379	0.379	0.380	0.380	0.380	0.381	0.382
Solution.....	0.6 cc. 1 *M* $NaHCO_3$ + 1.4 cc. 1 *M* Na_2CO_3 + 98 cc. H_2O	0.5 cc. 1 *M* $NaHCO_3$ + 1.5 cc. 1 *M* Na_2CO_3 + 98 cc. H_2O	0.4 cc. 1 *M* $NaHCO_3$ + 1.6 cc. 1 *M* Na_2CO_3 + 98 cc. H_2O	0.3 cc. 1 *M* $NaHCO_3$ + 1.7 cc. 1 *M* Na_2CO_3 + 98 cc. H_2O	0.2 cc. 1 *M* $NaHCO_3$ + 1.8 cc. 1 *M* Na_2CO_3 + 98 cc. H_2O	0.1 cc. 1 *M* $NaHCO_3$ +1.9 cc. 1 *M* Na_2CO_3 + 98 cc. H_2O	2.0 cc. 1 *M* Na_2CO_3 + 98 cc. H_2O
Hours in the solution.	Gain in parts, of one part of gelatin.						
5.5	6.50	6.30	6.50	6.34	6.10	6.51	6.35
29	12.60	12.00	12.13	12.16	12.21	12.00	12.35
53	14.01	13.27	13.35	13.52	13.60	13.14	13.50
Solution No...	(15)	(16)	(17)	(18)	(19)	(20)	(21)

Dry wt. of gelatin disc....	0.382	0.382	0.384	0.384	0.385	0.387	0.388
Solution.....	1.9 cc. 1 *M* Na_2CO_3 + 0.1 cc. 1 *N* NaOH + 98 cc. H_2O	1.8 cc. 1 *M* Na_2CO_3 + 0.2 cc. 1 *N* NaOH + 98 cc. H_2O	1.7 cc. 1 *M* Na_2CO_3 + 0.3 cc. 1 *N* NaOH + 98 cc. H_2O	1.6 cc. 1 *M* Na_2CO_3 + 0.4 cc. 1 *N* NaOH + 98 cc. H_2O	1.5 cc. 1 *M* Na_2CO_3 + 0.5 cc. 1 *N* NaOH + 98 cc. H_2O	1.4 cc. 1 *M* Na_2CO_3 + 0.6 cc. 1 *N* NaOH + 98 cc. H_2O	1.3 cc. 1 *M* Na_2CO_3 + 0.7 cc. 1 *N* NaOH + 98 cc. H_2O
Hours in the solution.	Gain in parts, of one part of gelatin.						
5.5	6.92	7.21	7.45	7.40	8.20	8.78	9.80
29	13.01	13.28	13.09	13.78	14.65	15.20	16.34
53	14.26	14.42	14.24	15.02	15.63	16.13	17.24
Solution No...	(22)	(23)	(24)	(25)	(26)	(27)	(28)

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TABLE XIV (*continued*).

Dry wt. of gelatin disc....	0.390	0.390	0.390	0.392	0.393	0.393	0.395
Solution.....	1.2 cc. 1 *M* Na_2CO_3 + 0.8 cc. 1 *N* NaOH + 98 cc. H_2O	1.1 cc. 1 *M* Na_2CO_3 + 0.9 cc. 1 *N* NaOH + 98 cc. H_2O	1 0 cc. 1 *M* Na_2CO_3 + 1.0 cc. 1 *N* NaOH + 98 cc. H_2O	0.9 cc. 1 *M* Na_2CO_3 + 1.1 cc. 1 *N* NaOH + 98 cc. H_2O	0.8 cc. 1 *M* Na_2CO_3 + 1.2 cc. 1 *N* NaOH + 98 cc. H_2O	0.7 cc. 1 *M* Na_2CO_3 + 1.3 cc. 1 *N* NaOH + 98 cc. H_2O	0.6 cc. 1 *M* Na_2CO_3 + 1.4 cc. 1 *N* NaOH + 98 cc. H_2O
Hours in the solution.	Gain in parts, of one part of gelatin.						
5.5	9.58	9.93	10.18	10.14	11.85	11.70	11.40
29	16.34	17.51	17.55	17.51	19.84	20.32	20.10
53	17.28	18.51	18.76	18.13	20.45	21.94	21.76
Solution No...	(29)	(30)	(31)	(32)	(33)	(34)	(35)

Dry wt. of gelatin disc....	0.395	0.396	0.396	0.396	0.397	0.397	0.368
Solution.....	0.5 cc. 1 *M* Na_2CO_3 + 1.5 cc. 1 *N* NaOH + 98 cc. H_2O	0.4 cc. 1 *M* Na_2CO_3 + 1.6 cc. 1 *N* NaOH + 98 cc. H_2O	0.3 cc. 1 *M* Na_2CO_3 + 1.7 cc. 1 *N* NaOH + 98 cc. H_2O	0.2 cc. 1 *M* Na_2CO_3 + 1.8 cc. 1 *N* NaOH + 98 cc. H_2O	0.1 cc. 1 *M* Na_2CO_3 + 1.9 cc. 1 *N* NaOH + 98 cc. H_2O	2.0 cc. 1 *N* NaOH + 98 cc. H_2O	100 cc. H_2O
Hours in the solution.	Gain in parts, of one part of gelatin.						
5.5	11.86	11.97	11.77	11.75	11.76	13.12	3.36
29	20.64	20.73	20.71	21.72	22.45	24.00	6.23
53	22.50	22.67	22.24	24.90	25.05	29.00	7.18
Solution No...	(36)	(37)	(38)	(39)	(40)	(41)	(H_2O)

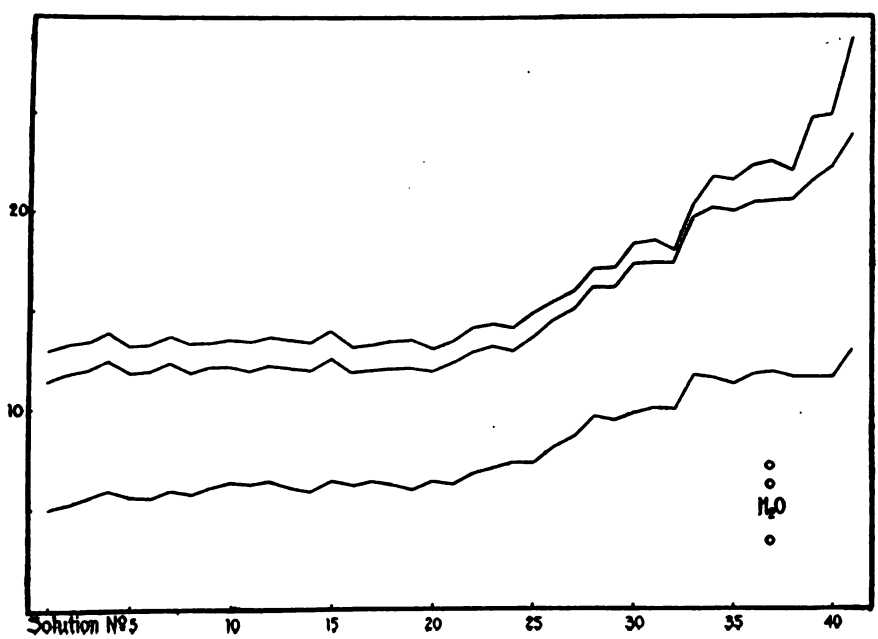

Fig. 14.

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Summary.

1. Experiments are described showing the amounts of water absorbed by gelatin discs immersed in different concentrations of the primary, binary or ternary salts of phosphoric, citric and carbonic acids. The swelling varies not only with the salt but with its concentration.

2. In further experiments are detailed the absorption of water in phosphate and citrate mixtures varying from the extreme of the pure acid on the one side through the mono-, di- and trisodium salts of these acids to pure sodium hydroxide on the other. Irrespective of the manner in which these mixtures are prepared (whether by progressive substitution of one salt for another, through the addition of the requisite acid to an alkali, through the addition of alkali to the proper acid, or through the addition of either acid or alkali to a given salt) it is found, when amount of water absorbed is plotted on the vertical and change in composition of the mixture on the horizontal, that the result yields a V-shaped or U-shaped curve. From a minimal point in the middle of this curve, there is a progressive increase in water absorption to the left or to the right as acid content or alkali content of the mixture is increased.

3. What has been said of phosphate and citrate mixtures holds also for carbonate mixtures.

4. These findings are held to be applicable to the problem of water absorption by protoplasm and to sustain the old contention that even in the presence of buffer salts there is an increase in water absorption (increased turgor or edema) with every increase in the acid (or alkali) content of the protein colloids found in the involved cell, organ or organism.

CINCINNATI, OHIO.

[CONTRIBUTION FROM THE EICHBERG LABORATORY OF PHYSIOLOGY IN THE UNIVERSITY OF CINCINNATI.]

ON THE SWELLING OF FIBRIN IN POLYBASIC ACIDS AND THEIR SALTS.

BY MARTIN H. FISCHER AND MARTIN BENZINGER.

Received November 2, 1917.

I.

It was shown in a previous paper[1] that water absorption by such a protein as gelatin increases even in the presence of so-called buffer salts with every increase in the acid or alkali content of the mixture on either side of a low point. This conclusion is contrary to much generally accepted opinion.[2] In order to show that the behavior of gelatin is not exceptional

[1] Martin H. Fischer and Marian O. Hooker, *Science*, **46**, 189 (1917); cf. preceding article.

[2] See Max Koppel, *Deut. Arch. klin. Med.*, **112**, 594 (1913); see also Henderson, Palmer and Newburgh, *J. Pharm. Exp. Therap.*, **5**, 449 (1914) as well as their numerous followers.

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the experiments detailed in this paper were undertaken. They show that the same general law holds for the absorption of water by another protein, namely fibrin. The fibrin was a preparation carefully prepared from blood and thoroughly washed to remove as many adhering salts as possible. After being dried at a low temperature it was pulverized in a mortar. Weighed amounts of the powder (0.5 g.) were then introduced into definite volumes (20 cc.) of the various solutions employed, contained in calibrated test tubes of uniform diameter (1.5 cm.). The same standard solutions of acids, alkali and of salts as were employed in the previous study were used in this one. All the mixtures in the various tubes were treated in exactly the same fashion, as to shaking, settling, etc. The height of the swollen fibrin columns, at the end of 24 hours, was taken as the index of water absorption. The results of our several series of experiments may be summed up as follows:

II.

(*a*) We tested first the effects of a progressive change from monosodium citrate through disodium citrate to trisodium citrate in equimolar concentrations, continuing the series toward a pure acid on the one side and toward a pure alkali upon the other side, as shown in Table I.

As indicated by the heights of the fibrin columns, and better by the curve of Fig. 1 which expresses the results of this experiment graphically, greatest swelling is observed in the pure solutions of acid or alkali. From these extremes the amount of swelling decreases as neutralization progresses until a low point is reached in the middle of the curve. This low point is observed in a mixture of, approximately, one molar equivalent of monosodium citrate with two molar equivalents of disodium citrate. In comparing this minimal point for fibrin with that obtained in the case of gelatin it is seen that in the latter instance it lies closer to the (theoretically) pure solution of monosodium citrate.

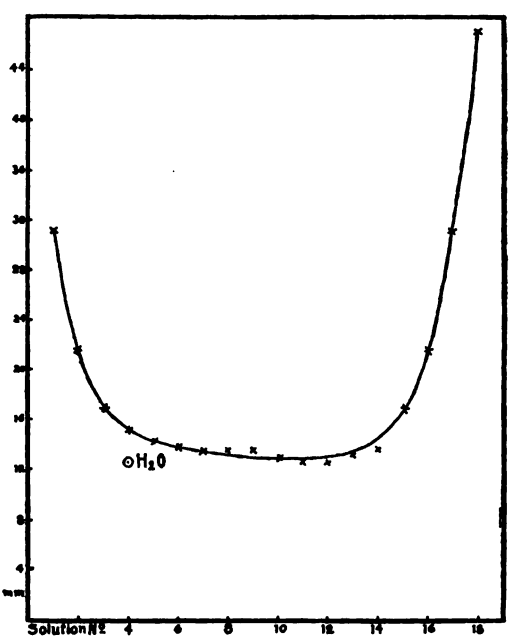

Fig. 1.

(*b*) In a next series of experiments we tested the effects of a gradual increase in the phosphoric acid content

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TABLE I.

Fibrin—*Citric Acid through Citrates to Sodium Hydroxide.*

Solution number.	Concentration of solution.	Height of fibrin column in mm. after 24 hours.
1	2 cc. 1 *N* citric acid +18 cc. H_2O	31.0
2	1.6 cc. 1 *N* citric acid +0.4 cc. 1 *M* monosodium citrate +18 cc. H_2O	21.5
3	1.2 cc. 1 *N* citric acid +0.8 cc. 1 *M* monosodium citrate +18 cc. H_2O	16.5
4	0.8 cc. 1 *N* citric acid +1.2 cc. 1 *M* monosodium citrate +18 cc. H_2O	15.0
5	0.4 cc. 1 *N* citric acid +1.6 cc. 1 *M* monosodium citrate +18 cc. H_2O	14.0
6	2 cc. 1 *M* monosodium citrate +18 cc. H_2O	14.0
7	1.6 cc 1 *M* monosodium citrate +0.4 cc. 1 *M* disodium citrate +18 cc. H_2O	13.5
8	1.2 cc. 1 *M* monosodium citrate +0.8 cc. 1 *M* disodium citrate +18 cc. H_2O	13.5
9	0.8 cc. 1 *M* monosodium citrate +1.2 cc. 1 *M* disodium citrate +18 cc. H_2O	13.5
10	0.4 cc. 1 *M* monosodium citrate +1.6 cc. 1 *M* disodium citrate +18 cc. H_2O	13.0
11	2 cc. 1 *M* disodium citrate +18 cc. H_2O	12.5
12	1.6 cc. 1 *M* disodium citrate +0.4 cc. 1 *M* trisodium citrate +18 cc. H_2O	12.5
13	1.2 cc. 1 *M* disodium citrate +0.8 cc. 1 *M* trisodium citrate +18 cc. H_2O	13.0
14	0.8 cc. 1 *M* disodium citrate +1.2 cc. 1 *M* trisodium citrate +18 cc. H_2O	13.5
15	0.4 cc. 1 *M* disodium citrate +1.6 cc. 1 *M* trisodium citrate +18 cc. H_2O	17.0
16	2 cc. 1 *M* trisodium citrate +18 cc. H_2O	21.5
17	1.6 cc. 1 *M* trisodium citrate +0.4 cc. 1 *N* NaOH +18 cc. H_2O	31.0
18	1.2 cc. 1 *M* trisodium citrate +0.8 cc. 1 *N* NaOH +18 cc. H_2O	47.0
19	0.8 cc. 1 *M* trisodium citrate +1.2 cc. 1 *N* NaOH +18 cc. H_2O	58.0
20	0.4 cc. 1 *M* trisodium citrate +1.6 cc. 1 *N* NaOH +18 cc. H_2O	73.0
21	2 cc. 1 *N* NaOH +18 cc. H_2O	96.5
22	20 cc. water (control)	12.5

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TABLE II.

Fibrin—*Disodium Phosphate + Increasing Amounts of Phosphoric Acid.*

Solution number.	Concentration of solution.	Height of fibrin column in mm. after 24 hours.
1	0.8 cc. 0.25 *M* Na_2HPO_4 + 0.44 cc. 1 *N* H_3PO_4 +18.76 cc. H_2O	20.0
2	0.8 cc. 0.25 *M* Na_2HPO_4 + 0.42 cc. 1 *N* H_3PO_4 +18.78 cc. H_2O	19.0
3	0.8 cc. 0.25 *M* Na_2HPO_4 + 0.40 cc. 1 *N* H_3PO_4 +18.80 cc. H_2O	18.0
4	0.8 cc. 0.25 *M* Na_2HPO_4 + 0.38 cc. 1 *N* H_3PO_4 +18.82 cc. H_2O	18.0
5	0.8 cc. 0.25 *M* Na_2HPO_4 + 0.36 cc. 1 *N* H_3PO_4 +18.84 cc. H_2O	18.0
6	0.8 cc. 0.25 *M* Na_2HPO_4 + 0.34 cc. 1 *N* H_3PO_4 +18.86 cc. H_2O	17.5
7	0.8 cc. 0.25 *M* Na_2HPO_4 + 0.32 cc. 1 *N* H_3PO_4 +18.88 cc. H_2O	17.0
8	0.8 cc. 0.25 *M* Na_2HPO_4 + 0.30 cc. 1 *N* H_3PO_4 +18.90 cc. H_2O	16.5
9	0.8 cc. 0.25 *M* Na_2HPO_4 + 0.28 cc. 1 *N* H_3PO_4 +18.92 cc. H_2O	15.5
10	0.8 cc. 0.25 *M* Na_2HPO_4 + 0.26 cc. 1 *N* H_3PO_4 +18.94 cc. H_2O	15.0
11	0.8 cc. 0.25 *M* Na_2HPO_4 + 0.24 cc. 1 *N* H_3PO_4 +18.96 cc. H_2O	14.5
12	0.8 cc. 0.25 *M* Na_2HPO_4 + 0.22 cc. 1 *N* H_3PO_4 +18.98 cc. H_2O	14.0
13	0.8 cc. 0.25 *M* Na_2HPO_4 + 0.20 cc. 1 *N* H_3PO_4 +19.00 cc. H_2O	14.0
14	0.8 cc. 0.25 *M* Na_2HPO_4 + 0.18 cc. 1 *N* H_3PO_4 +19.02 cc. H_2O	14.0
15	0.8 cc. 0.25 *M* Na_2HPO_4 + 0.16 cc. 1 *N* H_3PO_4 +19.04 cc. H_2O	13.5
16	0.8 cc. 0.25 *M* Na_2HPO_4 + 0.14 cc. 1 *N* H_3PO_4 +19.06 cc. H_2O	14.0
17	0.8 cc. 0.25 *M* Na_2HPO_4 + 0.12 cc. 1 *N* H_3PO_4 +19.08 cc. H_2O	14.0
18	0.8 cc. 0.25 *M* Na_2HPO_4 + 0.10 cc. 1 *N* H_3PO_4 +19.10 cc. H_2O	14.5
19	0.8 cc. 0.25 *M* Na_2HPO_4 + 0.08 cc. 1 *N* H_3PO_4 +19.12 cc. H_2O	14.5
20	0.8 cc. 0.25 *M* Na_2HPO_4 + 0.06 cc. 1 *N* H_3PO_4 +19.14 cc. H_2O	14.5
21	0.8 cc. 0.25 *M* Na_2HPO_4 + 0.04 cc. 1 *N* H_3PO_4 +19.16 cc. H_2O	14.5
22	0.8 cc. 0.25 *M* Na_2HPO_4 + 0.02 cc. 1 *N* H_3PO_4 +19.18 cc. H_2O	15.5
23	0.8 cc. 0.25 *M* Na_2HPO_4 +19.2 cc. H_2O	16.0
24	20 cc. water (control)	12.5

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of a solution containing a fixed amount of disodium phosphate. The results are shown in Table II and Fig. 2. When phosphoric acid is added to disodium phosphate there is at first a decrease in the amount of swelling. This gives way later to an increased swelling as the concentration of the acid passes a certain point. The experimental results show that this point of minimal swelling is observed in a mixture which theoretically is composed of about molar equivalents of disodium phosphate and monosodium phosphate.

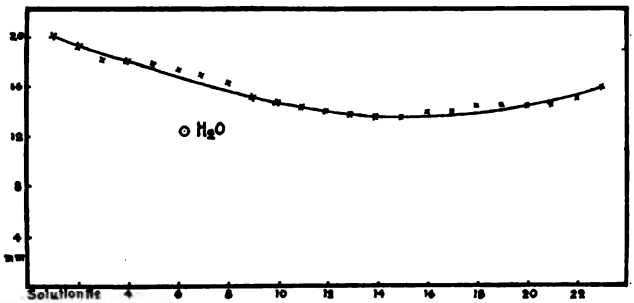

Fig. 2.

(*c*) In Table III and Fig. 3 are shown the effects of adding to the same concentration of disodium phosphate used in the previous experiment, progressively greater amounts of sodium hydroxide. There is, with every increase in the concentration of the added alkali, an increase in the height of the swelling column.

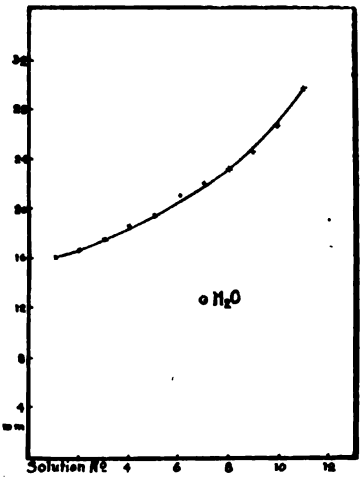

Fig. 3.

(*d*) The effects of adding progressively greater amounts of sodium hydroxide to a fixed amount of monosodium phosphate of the same molar concentration as the disodium phosphate used in the previous experiments are shown in Table IV and Fig. 4. When small amounts of the alkali are added to the monosodium phosphate there is to be observed at first a decrease in the amount of swelling which later, however, with further increase in the amount of alkali added, gives way to an increased swelling. It is again obvious that the low point in the swelling curve is found at a point at which the mixture is essentially one of molar equivalents of monosodium and disodium phosphate.

(*e*) The results of another type of variations in experimental procedure is shown in Table V and Fig. 5. Here a fixed amount of phosphoric acid has added to it progressively greater amounts of sodium hydroxide. This arrangement allows us to see the effects of simultaneously reducing acid content while increasing the amount and kind of phosphate present.

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TABLE III.

Fibrin—*Disodium Phosphate + Increasing Amounts of Sodium Hydroxide.*

Solution number.	Concentration of solution.	Height of fibrin column in mm. after 24 hours.
1	0.8 cc. 0.25 *M* Na_2HPO_4 +19.2 cc. H_2O	16.0
2	0.8 cc. 0.25 *M* Na_2HPO_4 + 0.02 cc. 1 *N* NaOH +19.18 cc. H_2O	16.5
3	0.8 cc. 0.25 *M* Na_2HPO_4 + 0.04 cc. 1 *N* NaOH +19.16 cc. H_2O	17.5
4	0.8 cc. 0.25 *M* Na_2HPO_4 + 0.06 cc. 1 *N* NaOH +19.14 cc. H_2O	18.5
5	0.8 cc. 0.25 *M* Na_2HPO_4 + 0.08 cc. 1 *N* NaOH +19.12 cc. H_2O	19.5
6	0.8 cc. 0.25 *M* Na_2HPO_4 + 0.10 cc. 1 *N* NaOH +19.10 cc. H_2O	21.0
7	0.8 cc. 0.25 *M* Na_2HPO_4 + 0.12 cc. 1 *N* NaOH +19.08 cc. H_2O	22.0
8	0.8 cc. 0.25 *M* Na_2HPO_4 + 0.14 cc. 1 *N* NaOH +19.06 cc. H_2O	23.0
9	0.8 cc. 0.25 *M* Na_2HPO_4 + 0.16 cc. 1 *N* NaOH +19.04 cc. H_2O	24.5
10	0.8 cc. 0.25 *M* Na_2HPO_4 + 0.18 cc. 1 *N* NaOH +19.02 cc. H_2O	26.5
11	0.8 cc. 0.25 *M* Na_2HPO_4 + 0.20 cc. 1 *N* NaOH +19.00 cc. H_2O	29.5
12	0.8 cc. 0.25 *M* Na_2HPO_4 + 0.22 cc. 1 *N* NaOH +18.98 cc. H_2O	34.5
13	20 cc. water (control)	12.5

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TABLE IV.

Fibrin—*Monosodium Phosphate + Increasing Amounts of Sodium Hydroxide.*

Solution number.	Concentration of solution.	Height of fibrin column in mm. after 24 hours.
1	0.2 cc. 1 *M* NaH_2PO_4 +19.08 cc. H_2O	16.0
2	0.2 cc. 1 *M* NaH_2PO_4 + 0.02 cc. 1 *N* NaOH +19.78 cc. H_2O	15.5
3	0.2 cc. 1 *M* NaH_2PO_4 + 0.04 cc. 1 *N* NaOH +19.76 cc. H_2O	15.5
4	0.2 cc. 1 *M* NaH_2PO_4 + 0.06 cc. 1 *N* NaOH +19.74 cc. H_2O	15.5
5	0.2 cc. 1 *M* NaH_2PO_4 + 0.08 cc. 1 *N* NaOH +19.72 cc. H_2O	15.0
6	0.2 cc. 1 *M* NaH_2PO_4 + 0.10 cc. 1 *N* NaOH +19.70 cc. H_2O	15.0
7	0.2 cc. 1 *M* NaH_2PO_4 + 0.12 cc. 1 *N* NaOH +19.68 cc. H_2O	14.0
8	0.2 cc. 1 *M* NaH_2PO_4 + 0.14 cc. 1 *N* NaOH +19.66 cc. H_2O	15.0
9	0.2 cc. 1 *M* NaH_2PO_4 + 0.16 cc. 1 *N* NaOH +19.64 cc. H_2O	15.5
10	0.2 cc. 1 *M* NaH_2PO_4 + 0.18 cc. 1 *N* NaOH +19.62 cc. H_2O	15.5
11	0.2 cc. 1 *M* NaH_2PO_4 + 0.20 cc. 1 *N* NaOH +19.60 cc. H_2O	15.5
12	0.2 cc. 1 *M* NaH_2PO_4 + 0.22 cc. 1 *N* NaOH +19.58 cc. H_2O	16.0
13	0.2 cc. 1 *M* NaH_2PO_4 + 0.24 cc. 1 *N* NaOH +19.56 cc. H_2O	16.5
14	0.2 cc. 1 *M* NaH_2PO_4 + 0.26 cc. 1 *N* NaOH +19.54 cc. H_2O	18.0
15	0.2 cc. 1 *M* NaH_2PO_4 + 0.28 cc. 1 *N* NaOH +19.52 cc. H_2O	19.5
16	0.2 cc. 1 *M* NaH_2PO_4 + 0.30 cc. 1 *N* NaOH +19.50 cc. H_2O	21.5
17	0.2 cc. 1 *M* NaH_2PO_4 + 0.32 cc. 1 *N* NaOH +19.48 cc. H_2O	23.5
18	0.2 cc. 1 *M* NaH_2PO_4 + 0.34 cc. 1 *N* NaOH +19.46 cc. H_2O	25.0
19	0.2 cc. 1 *M* NaH_2PO_4 + 0.36 cc. 1 *N* NaOH +19.44 cc. H_2O	27.5
20	0.2 cc. 1 *M* NaH_2PO_4 + 0.38 cc. 1 *N* NaOH +19.42 cc. H_2O	33.0
21	20 cc. water (control)	12.5

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The result is again, however, a curve of the same general type already discussed. Beginning with the greatest swelling in the pure acid there is a gradual fall in the curve until a low point is reached in a mixture lying midway between the (theoretically) pure monosodium phosphate and the pure disodium phosphate. From this point represented by the pure disodium phosphate the swelling then increases more abruptly as we enter the realm of the pure trisodium phosphate or this plus unneutralized alkali.

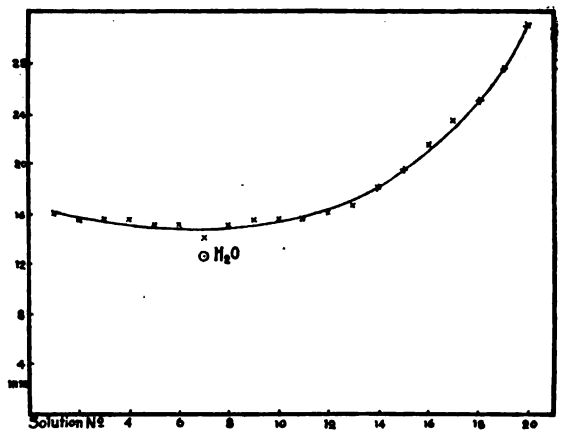

Fig. 4.

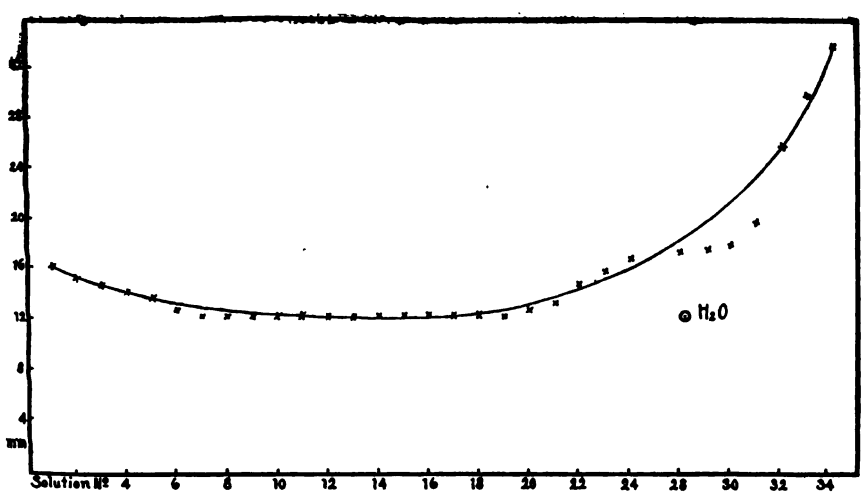

Fig. 5.

(*f*) A final type of variations in experimental procedure is shown in Table VI and Fig. 6. Here a fixed amount of alkali has added to it progressively greater amounts of phosphoric acid until neutralization is carried to the point of getting a (theoretically) pure solution of trisodium phosphate. The progressive decrease in the amount of swelling with decrease in alkalinity and increase in phosphate content is readily apparent.

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TABLE V.

Fibrin—*Phosphoric Acid + Increasing Amounts of Sodium Hydroxide.*

Solution number.	Concentration of solution.	Height of fibrin column in mm. after 24 hours.
1	0.6 cc. 1 *N* H_3PO_4 +0.02 cc. 1 *N* NaOH +19.38 cc. H_2O	16.5
2	0.6 cc. 1 *N* H_3PO_4 +0.04 cc. 1 *N* NaOH +19.36 cc. H_2O	15.5
3	0.6 cc. 1 *N* H_3PO_4 +0.06 cc. 1 *N* NaOH +19.34 cc. H_2O	15.0
4	0.6 cc. 1 *N* H_3PO_4 +0.08 cc. 1 *N* NaOH +19.32 cc. H_2O	14.5
5	0.6 cc. 1 *N* H_3PO_4 +0.10 cc. 1 *N* NaOH +19.30 cc. H_2O	14.0
6	0.6 cc. 1 *N* H_3PO_4 +0.12 cc. 1 *N* NaOH +19.28 cc. H_2O	13.0
7	0.6 cc. 1 *N* H_3PO_4 +0.14 cc. 1 *N* NaOH +19.26 cc. H_2O	12.5
8	0.6 cc. 1 *N* H_3PO_4 +0.16 cc. 1 *N* NaOH +19.24 cc. H_2O	12.5
9	0.6 cc. 1 *N* H_3PO_4 +0.18 cc. 1 *N* NaOH +19.22 cc. H_2O	12.5
10	0.6 cc. 1 *N* H_3PO_4 +0.20 cc. 1 *N* NaOH +19.20 cc. H_2O	12.5
11	0.6 cc. 1 *N* H_3PO_4 +0.22 cc. 1 *N* NaOH +19.18 cc. H_2O	12.5
12	0.6 cc. 1 *N* H_3PO_4 +0.24 cc. 1 *N* NaOH +19.16 cc. H_2O	12.5
13	0.6 cc. 1 *N* H_3PO_4 +0.26 cc. 1 *N* NaOH +19.14 cc. H_2O	12.5
14	0.6 cc. 1 *N* H_3PO_4 +0.28 cc. 1 *N* NaOH +19.12 cc. H_2O	12.5
15	0.6 cc. 1 *N* H_3PO_4 +0.30 cc. 1 *N* NaOH +19.10 cc. H_2O	12.5
16	0.6 cc. 1 *N* H_3PO_4 +0.32 cc. 1 *N* NaOH +19.08 cc. H_2O	12.5
17	0.6 cc. 1 *N* H_3PO_4 +0.34 cc. 1 *N* NaOH +19.06 cc. H_2O	12.5
18	0.6 cc. 1 *N* H_3PO_4 +0.36 cc. 1 *N* NaOH +19.04 cc. H_2O	12.5
19	0.6 cc. 1 *N* H_3PO_4 +0.38 cc. 1 *N* NaOH +19.02 cc. H_2O	12.5
20	0.6 cc. 1 *N* H_3PO_4 +0.40 cc. 1 *N* NaOH +19.00 cc. H_2O	13.0
21	0.6 cc. 1 *N* H_3PO_4 +0.42 cc. 1 *N* NaOH +18.98 cc. H_2O	14.5
22	0.6 cc. 1 *N* H_3PO_4 +0.44 cc. 1 *N* NaOH +18.96 cc. H_2O	15.0
23	0.6 cc. 1 *N* H_3PO_4 +0.46 cc. 1 *N* NaOH +18.94 cc. H_2O	16.0
24	0.6 cc. 1 *N* H_3PO_4 +0.48 cc. 1 *N* NaOH +18.92 cc. H_2O	17.0
25	0.6 cc. 1 *N* H_3PO_4 +0.50 cc. 1 *N* NaOH +18.90 cc. H_2O	75.0(?)
26	0.6 cc. 1 *N* H_3PO_4 +0.52 cc. 1 *N* NaOH +18.88 cc. H_2O	17.5
27	0.6 cc. 1 *N* H_3PO_4 +0.54 cc. 1 *N* NaOH +18.86 cc. H_2O	17.5
28	0.6 cc. 1 *N* H_3PO_4 +0.56 cc. 1 *N* NaOH +18.84 cc. H_2O	18.0
29	0.6 cc. 1 *N* H_3PO_4 +0.58 cc. 1 *N* NaOH +18.82 cc. H_2O	20.0
30	0.6 cc. 1 *N* H_3PO_4 +0.60 cc. 1 *N* NaOH +18.80 cc. H_2O	26.0
31	0.6 cc. 1 *N* H_3PO_4 +0.62 cc. 1 *N* NaOH +18.78 cc. H_2O	[illegible]
[illegible]	[illegible] 1 *N* H_3PO_4 +[illegible] 1 *N* NaOH [illegible] H_2O	[illegible]

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TABLE VI.

Fibrin—*Sodium Hydroxide + Increasing Amounts of Phosphoric Acid.*

Solution number.	Concentration of solution.	Height of fibrin column in mm. after 24 hours
1	0.6 cc. 1 *N* NaOH +0.06 cc. 1 *N* H_3PO_4 +18.80 cc. H_2O	23.0
2	0.6 cc. 1 *N* NaOH +0.58 cc. 1 *N* H_3PO_4 +18.82 cc. H_2O	23.5
3	0.6 cc. 1 *N* NaOH +0.54 cc. 1 *N* H_3PO_4 +18.86 cc. H_2O	25.5
4	0.6 cc. 1 *N* NaOH +0.50 cc. 1 *N* H_3PO_4 +18.90 cc. H_2O	28.0
5	0.6 cc. 1 *N* NaOH +0.46 cc. 1 *N* H_3PO_4 +18.94 cc. H_2O	32.5
6	0.6 cc. 1 *N* NaOH +0.42 cc. 1 *N* H_3PO_4 +18.98 cc. H_2O	35.5
7	0.6 cc. 1 *N* NaOH +0.38 cc. 1 *N* H_3PO_4 +19.02 cc. H_2O	40.5
8	0.6 cc. 1 *N* NaOH +0.34 cc. 1 *N* H_3PO_4 +19.06 cc. H_2O	47.0
9	0.6 cc. 1 *N* NaOH +0.30 cc. 1 *N* H_3PO_4 +19.10 cc. H_2O	45.0
10	0.6 cc. 1 *N* NaOH +0.26 cc. 1 *N* H_3PO_4 +19.14 cc. H_2O	47.5
11	0.6 cc. 1 *N* NaOH +0.22 cc. 1 *N* H_3PO_4 +19.18 cc. H_2O	52.0
12	0.6 cc. 1 *N* NaOH +0.18 cc. 1 *N* H_3PO_4 +19.22 cc. H_2O	59.0
13	0.6 cc. 1 *N* NaOH +0.14 cc. 1 *N* H_3PO_4 +19.26 cc. H_2O	62.0
14	0.6 cc. 1 *N* NaOH +0.10 cc. 1 *N* H_3PO_4 +19.30 cc. H_2O	63.5
15	0.6 cc. 1 *N* NaOH +0.06 cc. 1 *N* H_3PO_4 +19.34 cc. H_2O	68.0
16	0.6 cc. 1 *N* NaOH +0.02 cc. 1 *N* H_3PO_4 +19.38 cc. H_2O	75.0
17	20 cc. water (control)	12.5

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III.

The experimental findings detailed in this note, with those previously published in the case of gelatin, bring out the fact that the minimal points of water absorption in citrate and phosphate mixtures are different in the cases of gelatin and fibrin. While the minimal swelling point for gelatin is found in a mixture closely approximating one of pure monosodium citrate or pure monosodium phosphate, the minimal one for fibrin is found at a point represented more nearly by a mixture of molar equivalents of the mono- and di- salts of these two acids. Such differences in the behavior of various proteins must be kept in mind when these experiments on simple protein colloids are applied to biological material. Protoplasm represents, according to our present notion, a mixture of at least two and probably several different proteins.

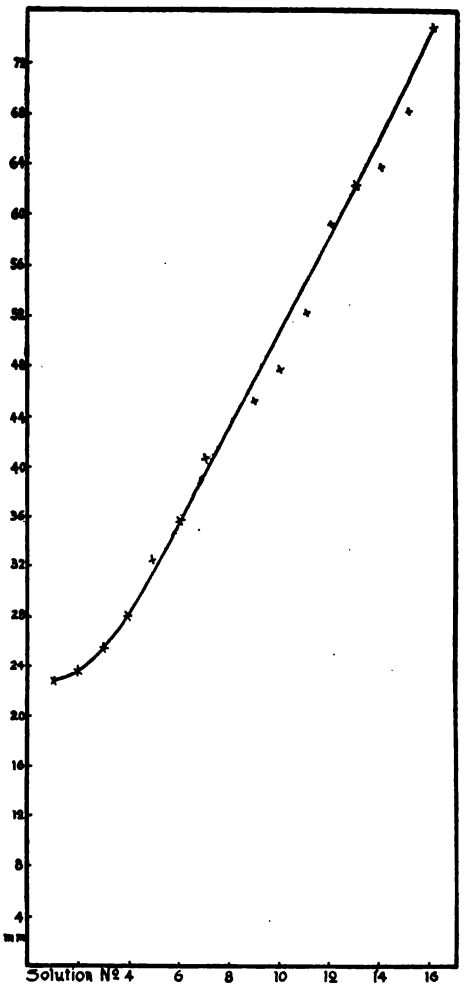

Fig. 6.

We hold that the results of this study, with those previously detailed upon the swelling of gelatin in polybasic acids and their salts, corroborate and amplify ideas previously expressed regarding the importance of acids, of alkalies, of various salts, and of these in mixture in determining the amount of water absorbed by protoplasm under physiological and pathological conditions. The well-established qualitative and quantitative analogies between the absorption of water by various hydrophilic colloids (like the proteins) and isolated cells, organs or organisms, whether of animal or vegetable origin, show that the problem of water absorption is essentially a colloid-chemical phenomenon. These studies with polybasic acids and their salts permit us to re-emphasize the importance of an abnormal production or accumulation of acids within such colloid systems for increasing the

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amount of water thus held and this independently of the fact that such accumulation of acid may occur in the presence or in the absence of so-called "buffer" salts. Through the accumulation or production in protoplasm of an abnormally great amount of acid (or of alkali), we are thus enabled to explain the mechanism by which the abnormally high hydrations of living cells are brought about as such are observed in the excessive turgors of plant tissues, in the edemas which involve the animal body, or in those "diseases", which are in essence only edemas of certain organs, like nephritis (edema of the kidney), glaucoma (edema of the eye), or "uremia" (edema of the brain).

CINCINNATI, OHIO.

[CONTRIBUTION FROM THE EICHBERG LABORATORY OF PHYSIOLOGY IN THE UNIVERSITY OF CINCINNATI.]

ON THE LIQUEFACTION OR "SOLUTION" OF GELATIN IN POLYBASIC ACIDS AND THEIR SALTS.

BY MARTIN H. FISCHER AND WARD D. COFFMAN.

Received November 12, 1917.

I. Introduction.

The importance of the swelling and of the liquefaction or "solution" of a protein colloid for the interpretation of numerous biological or technological processes has been repeatedly emphasized.[1] Since the laws which govern the absorption of water by simple colloids (like the proteins) and those which govern the absorption of water by animal and plant tissues are identical, it is now easy to explain upon a colloid-chemical basis both the normal and the abnormal water contents of cells and tissues as observed under physiological and pathological circumstances and variously designated turgor, plasmoptysis and edema. On the other hand, the changes characteristic of the liquefaction or "solution" of a previously solid colloid (as when gelatin liquefies with rise of temperature) may be and have been called upon to explain the "solution" of some or all of the colloid constituents found in cells, thus accounting for the "softening" of the involved organs as well as for the appearance of the traces of colloids found in many normal "secretions" or the larger amount of such colloids found "dissolved" under pathological circumstances in the fluids bathing swollen or edematous tissues as exemplified, for instance, in the higher albumin content of urine coming from a swollen kidney, in that of the cerebral fluid covering a swollen brain, etc.

More simply stated, excessive turgor, plasmoptysis and edema are therefore to be defined as states of increased hydration (solvation) of the body colloids; and albuminuria, excessive protein content of spinal cord fluid, etc., as states of increased "solubility" of these colloids.

[1] Martin H. Fischer, "Edema and Nephritis," Ed. 2, New York, 1915, where references to the older literature on this subject may be found.

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The causes which may bring about a swelling of the involved tissues or their liquefaction or "solution" may in turn be found in those circumstances which are capable of bringing about these physicochemical changes in such colloids as constitute protoplasm. As of dominant importance in this matter an abnormal production or accumulation of acid in the pathologically involved tissues has been given first emphasis, though this is not by any means to be looked upon as the only cause for the observed colloid-chemical changes. In the case of the proteins, for example, the alkalies, the amines, pyridin and urea produce the same types of changes.

Because in protoplasm increased hydration (solvation) and liquefaction or "solution" of the involved colloids are almost constantly associated with each other it was suggested from the first that a common cause undoubtedly lay behind both processes. This conclusion has been repeatedly verified both in experiments upon simple colloids and upon animals. Proteins, for example, not only swell and go into solution under the influence of acids, but acid intoxications in animals not only make these swell (develop an edema) but cause their organs to "dissolve" (make albumin appear in the urine, for instance).

It is a commonly accepted view that this liquefaction or "solution" of a protein is but the extreme of what in lesser degree is called swelling, but, as pointed out in previous papers[1] *the swelling of a protein and its liquefaction or "solution" are totally different processes.* When one works with gelatin at concentrations and temperatures near its gelation or melting point, it can easily be shown that *the phenomena of hydration (swelling) and of "solution" while frequently associated are essentially different. Hydration is to be regarded as a change through which the protein enters into physicochemical combination with its solvent (water); "solution," as one which can be most easily understood at the present time as the expression of an increase in the degree of dispersion of the colloid.*

Since our previous experiments on the liquefaction or "solution" of gelatin in acids or alkalies with or without the simultaneous presence of various neutral salts might have voiced against them the same criticisms which have been raised against our experiments on swelling, namely, that the effects of the acids and alkalies were not tried out in the presence of "buffer" salts and so could not be applied to the living organism, we ran experiments on the solution of gelatin in parallel with those previously published[2] on the swelling of gelatin in various polybasic acids and their salts. As the following experimental facts show, *there is a progressive increase in the tendency of gelatin to go into solution in mixtures of the salts*

[1] Martin H. Fischer, "Edema and Nephritis," Ed. 2, 433, 444, New York, 1915; *Science*, **42**, 223 (1915); *Kolloid Z.*, **17**, 1 (1915).

[2] Martin H. Fischer and Marian O. Hooker, *Science*, **46**, 189 (1917).

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of polybasic acids as the amount of acid or alkali in these mixtures is increased from a given low point.

II. Experiments.

The same gelatin was used in these experiments as was used in our previous ones. Its quality was of such high grade that an 0.8% solution of the stock gelatin would set into a solid mass when left to itself for a few hours at 25°. To make sure of a stiff gelatin mixture we used a concentration well above this, *viz.*, 1% gelatin and set the thermostat for 20°. It should be added that all the tubes and their contents were treated in exactly the same fashion as to methods of mixing, exposure to heat or other influences which might change temporarily their gelation characteristics, etc.

In Table I are shown the effects of a progressive change from the extreme of a pure phosphoric acid through equimolar concentrations of mono-, di- and trisodium phosphate to pure sodium hydroxide upon the physical state of a fixed amount of gelatin contained in a unit volume of solvent. The maintenance of solidity by the gelatin in the middle of the series with progressive increase in fluidity to the left or to the right of this middle point can be more easily observed in the actual experiments than can be described in words or shown in such a photograph as that of Fig. 1. From

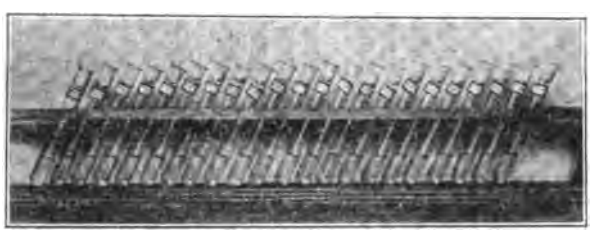

Fig. 1.

so stiff a gelatin that it vibrates when the tube is touched in the middle of the series, we pass through gelatins on either side of this which show the first evidences of a tendency to flow, to the end members which are almost as fluid as thin soup. The change from the solid to the fluid state may be observed in Fig. 1 by noting the line of the meniscus in the tubes; while on slanting the tubes this remains fixed and therefore forms an angle with the horizontal in the middle of the series, it assumes a horizontal position as we approach either end.

Since the concentration of the phosphate in Table I is about ten times that observed, for instance, in the tissues of the human body, we did a second series at a lower concentration of the phosphate and at one more nearly corresponding to physiological conditions. The results so far as maintenance of solidity or liquefaction of the gelatin is concerned are,

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TABLE I.

Gelatin—Phosphoric acid through phosphates to sodium hydroxide.

Solution number.	Mixture.	Physical state.
(1)	5 cc. 2% gel. +5.0 cc. H_2O (control)	solid
(2)	5 cc. 2% gel. +1.0 cc. 1 *N* H_3PO_4 +4.0 cc. H_2O	liquid
(3)	5 cc. 2% gel. +0.8 cc. 1 *N* H_3PO_4 +0.2 cc. 1 *M* monosod. phos. +4 cc. H_2O	liquid
(4)	5 cc. 2% gel. +0.6 cc. 1 *N* H_3PO_4 +0.4 cc. 1 *M* monosod. phos. +4 cc. H_2O	semi-solid
(5)	5 cc. 2% gel. +0.4 cc. 1 *N* H_3PO_4 +0.6 cc. 1 *M* monosod. phos. +4 cc. H_2O	semi-solid
(6)	5 cc. 2% gel. +0.2 cc. 1 *N* H_3PO_4 +0.8 cc. 1 *M* monosod. phos. +4 cc. H_2O	solid
(7)	5 cc. 2% gel. +1.0 cc. 1 *M* NaH_2PO_4 +4.0 cc. H_2O	solid
(8)	5 cc. 2% gel. +0.8 cc. 1 *M* NaH_2PO_4 +0.2 cc. 1 *M* Na_2HPO_4 +4 cc. H_2O	solid
(9)	5 cc. 2% gel. +0.6 cc. 1 *M* NaH_2PO_4 +0.4 cc. 1 *M* Na_2HPO_4 +4 cc. H_2O	solid
(10)	5 cc. 2% gel. +0.4 cc. 1 *M* NaH_2PO_4 +0.6 cc. 1 *M* Na_2HPO_4 +4 cc. H_2O	solid
(11)	5 cc. 2% gel. +0.2 cc. 1 *M* NaH_2PO_4 +0.8 cc. 1 *M* Na_2HPO_4 +4 cc. H_2O	solid
(12)	5 cc. 2% gel. +1.0 cc. 1 *M* Na_2HPO_4 +4.0 cc. H_2O	solid
(13)	5 cc. 2% gel. +0.8 cc. 1 *M* Na_2HPO_4 +0.2 cc. 1 *M* Na_3PO_4 +4 cc. H_2O	solid
(14)	5 cc. 2% gel. +0.6 cc. 1 *M* Na_2HPO_4 +0.4 cc. 1 *M* Na_3PO_4 +4 cc. H_2O	solid
(15)	5 cc. 2% gel. +0.4 cc. 1 *M* Na_2HPO_4 +0.6 cc. 1 *M* Na_3PO_4 +4 cc. H_2O	semi-solid
(16)	5 cc. 2% gel. +0.2 cc. 1 *M* Na_2HPO_4 +0.8 cc. 1 *M* Na_3PO_4 +4 cc. H_2O	liquid
(17)	5 cc. 2% gel. +1.0 cc. 1 *M* Na_3PO_4 +4.0 cc. H_2O	liquid
(18)	5 cc. 2% gel. +0.8 cc. 1 *M* Na_3PO_4 +0.2 cc. 1 *N* NaOH +4 cc. H_2O	liquid
(19)	5 cc. 2% gel. +0.6 cc. 1 *M* Na_3PO_4 +0.4 cc. 1 *N* NaOH +4 cc. H_2O	liquid
(20)	5 cc. 2% gel. +0.4 cc. 1 *M* Na_3PO_4 +0.6 cc. 1 *N* NaOH +4 cc. H_2O	liquid
(21)	5 cc. 2% gel. +0.2 cc. 1 *M* Na_3PO_4 +0.8 cc. 1 *N* NaOH +4 cc. H_2O	liquid
(22)	5 cc. 2% gel. +1.0 cc. 1 *N* NaOH + 4 cc. H_2O	liquid

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TABLE II.

Gelatin—Phosphoric acid through phosphates to sodium hydroxide.

Solution number.	Mixture.	Physical state.
(1)	5 cc. 2% gel. +5.0 cc. H_2O (control)	solid
(2)	5 cc. 2% gel. +0.10 cc. 1 *N* H_3PO_4 +4.90 cc. H_2O	liquid
(3)	5 cc. 2% gel. +0.08 cc. 1 *N* H_3PO_4 +0.02 cc. 1 *M* NaH_2PO_4 +4.9 cc. H_2O	liquid
(4)	5 cc. 2% gel. +0.06 cc. 1 *N* H_3PO_4 +0.04 cc. 1 *M* NaH_2PO_4 +4.9 cc. H_2O	semi-solid
(5)	5 cc. 2% gel. +0.04 cc. 1 *N* H_3PO_4 +0.06 cc. 1 *M* NaH_2PO_4 +4.9 cc. H_2O	semi-solid
(6)	5 cc. 2% gel. +0.02 cc. 1 *N* H_3PO_4 +0.08 cc. 1 *M* NaH_2PO_4 +4.9 cc. H_2O	solid
(7)	5 cc. 2% gel. +0.10 cc. 1 *M* NaH_2PO_4 +4.90 cc. H_2O	solid
(8)	5 cc. 2% gel. +0.08 cc. 1 *M* NaH_2PO_4 +0.02 cc. 1 *M* Na_2HPO_4 +4.9 cc. H_2O	solid
(9)	5 cc. 2% gel. +0.06 cc. 1 *M* NaH_2PO_4 +0.04 cc. 1 *M* Na_2HPO_4 +4.9 cc. H_2O	solid
(10)	5 cc. 2% gel. +0.04 cc. 1 *M* NaH_2PO_4 +0.06 cc. 1 *M* Na_2HPO_4 +4.9 cc. H_2O	solid
(11)	5 cc. 2% gel. +0.02 cc. 1 *M* NaH_2PO_4 +0.08 cc. 1 *M* Na_2HPO_4 +4.9 cc. H_2O	solid
(12)	5 cc. 2% gel. +0.10 cc. 1 *M* Na_2HPO_4 +4.90 cc. H_2O	solid
(13)	5 cc. 2% gel. +0.08 cc. 1 *M* Na_2HPO_4 +0.02 cc. 1 *M* Na_3PO_4 +4.9 cc. H_2O	solid
(14)	5 cc. 2% gel. +0.06 cc. 1 *M* Na_2HPO_4 +0.04 cc. 1 *M* Na_3PO_4 +4.9 cc. H_2O	solid
(15)	5 cc. 2% gel. +0.04 cc. 1 *M* Na_2HPO_4 +0.06 cc. 1 *M* Na_3PO_4 +4.9 cc. H_2O	semi-solid
(16)	5 cc. 2% gel. +0.02 cc. 1 *M* Na_2HPO_4 +0.08 cc. 1 *M* Na_3PO_4 +4.9 cc. H_2O	semi-solid
(17)	5 cc. 2% gel. +0.10 cc. 1 *M* Na_3PO_4 +4.90 cc. H_2O	semi-solid
(18)	5 cc. 2% gel. +0.08 cc. 1 *M* Na_3PO_4 +0.02 cc. 1 *N* NaOH +4.9 cc. H_2O	liquid
(19)	5 cc. 2% gel. +0.06 cc. 1 *M* Na_3PO_4 +0.04 cc. 1 *N* NaOH +4.9 cc. H_2O	liquid
(20)	5 cc. 2% gel. +0.04 cc. 1 *M* Na_3PO_4 +0.06 cc. 1 *N* NaOH +4.9 cc. H_2O	liquid
(21)	5 cc. 2% gel. +0.02 cc. 1 *M* Na_3PO_4 +0.08 cc. 1 *N* NaOH +4.9 cc. H_2O	liquid
(22)	5 cc. 2% gel. +0.10 cc. 1 *N* NaOH +4.9 cc. H_2O	liquid

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however, as shown in Table II, identical with those previously described in connection with Table I.

As an example of another polybasic acid commonly found in living protoplasm, we chose citric acid, studying its effects by noting the results incident to progressive change from citric acid through mono-, di- and trisodium citrate in equimolar concentrations to pure sodium hydroxide.

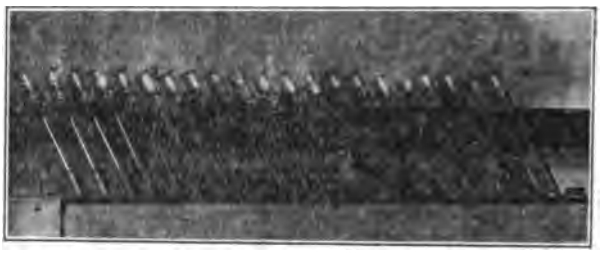

Fig. 2.

As shown in Table III, and Fig. 2, gelatin again remains solid in the middle of such a series and tends to liquefy as we pass toward the acid or alkaline extreme.

In Table IV and Fig. 3 are shown the effects of progressive change from sodium bicarbonate through sodium carbonate to sodium hydroxide. The carbonates in the concentrations indicated in this table showed a greater tendency to liquefy the gelatin than was observed in the phosphate

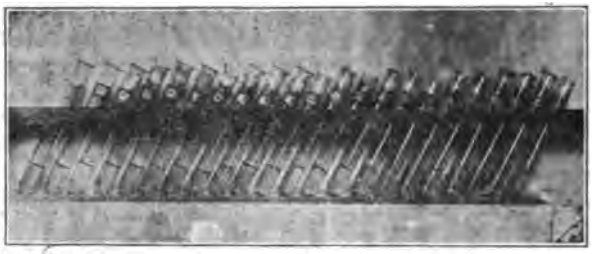

Fig. 3.

or citrate mixtures previously discussed. To show the effects of the different salt mixtures, this series of experiments was therefore kept at a somewhat lower temperature, namely, 5° C. At this temperature the gelatin remains solid in the pure sodium bicarbonate but tends to liquefy as this is replaced by carbonate or the carbonate by pure sodium hydroxide.

III. Remarks.

These experiments bring further proof that the hydration and the "solution" of a protein are not the same thing. Were solution merely the continuation of hydration then a liquid gelatin near the gelatin point

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TABLE III.

Gelatin—Citric acid through citrates to sodium hydroxide.

Solution number.	Mixture.	Physical state.
(X)	5 cc. 2% gel. +5.0 cc. H_2O (control)	solid
(1)	5 cc. 2% gel. +1.0 cc. 1 *N* citric acid +4.0 cc. H_2O	liquid
(2)	5 cc. 2% gel. +0.8 cc. 1 *N* citric acid +0.8 cc. 0.25 *M* monosod. cit. +3.4 cc. H_2O	semi-solid
(3)	5 cc. 2% gel. +0.6 cc. 1 *N* citric acid +1.6 cc. 0.25 *M* monosod. cit. +2.8 cc. H_2O	solid
(4)	5 cc. 2% gel. +0.4 cc. 1 *N* citric acid +2.4 cc. 0.25 *M* monosod. cit. +2.2 cc. H_2O	solid
(5)	5 cc. 2% gel +0.2 cc. 1 *N* citric acid +3.2 cc. 0.25 *M* monosod. cit. +1.6 cc. H_2O	solid
(6)	5 cc. 2% gel. +4.0 cc. 0.25 *M* monosod. cit. +1.0 cc. H_2O	solid
(7)	5 cc. 2% gel. +3.2 cc. 0.25 *M* monosod. cit. +0.8 cc. 0.25 *M* disod. cit. +1.0 cc. H_2O	solid
(8)	5 cc. 2% gel. +2.4 cc. 0.25 *M* monosod. cit. +1.6 cc. 0.25 *M* disod. cit. +1.0 cc. H_2O	solid
(9)	5 cc. 2% gel. +1.6 cc. 0.25 *M* monosod. cit. +2.4 cc. 0.25 *M* disod. cit. +1.0 cc. H_2O	solid
(10)	5 cc. 2% gel. +0.8 cc. 0.25 *M* monosod. cit. +3.2 cc. 0.25 *M* disod. cit. +1.0 cc. H_2O	solid
(11)	5 cc. 2% gel. +4.0 cc. 0.25 *M* disod. cit. +1.0 cc. H_2O	solid
(12)	5 cc. 2% gel. +3.2 cc. 0.25 *M* disod. cit. +0.8 cc. 0.25 *M* trisod. cit. +1.0 cc. H_2O	solid
(13)	5 cc. 2% gel. +2.4 cc. 0.25 *M* disod. cit. +1.6 cc. 0.25 *M* trisod. cit. +1.0 cc. H_2O	solid
(14)	5 cc. 2% gel. +1.6 cc. 0.25 *M* disod. cit. +2.4 cc. 0.25 *M* trisod. cit. +1.0 cc. H_2O	solid
(15)	5 cc. 2% gel. +0.8 cc. 0.25 *M* disod. cit. +3.2 cc. 0.25 *M* trisod. cit. +1.0 cc. H_2O	solid
(16)	5 cc. 2% gel. +4.0 cc. 0.25 *M* trisod. cit. +1.0 cc. H_2O	solid
(17)	5 cc. 2% gel. +3.2 cc. 0.25 *M* trisod. cit. +0.8 cc. 1 *N* NaOH +1.0 cc. H_2O	liquid
(18)	5 cc. 2% gel. +2.4 cc. 0.25 *M* trisod. cit. +1.6 cc. 1 *N* NaOH +1.0 cc. H_2O	liquid
(19)	5 cc. 2% gel. +1.6 cc. 0.25 *M* trisod. cit. +2.4 cc. 1 *N* NaOH +1.0 cc. H_2O	liquid
(20)	5 cc. 2% gel. +0.8 cc. 0.25 *M* trisod. cit. +3.2 cc. 1 *N* NaOH +1.0 cc. H_2O	liquid
(21)	5 cc. 2% gel. +4.0 cc. 1 *N* NaOH +1.0 cc. H_2O	liquid

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TABLE IV.

Gelatin—Sodium bicarbonate through sodium carbonate to sodium hydroxide.

Solution number.	Mixture.	Physical state.
(X)	5 cc. 2% gel. +5.00 cc. H_2O (control)	solid
(1)	5 cc. 2% gel. +0.20 cc. 1 *M* $NaHCO_3$ +4.80 cc. H_2O	solid
(2)	5 cc. 2% gel. +0.18 cc. 1 *M* $NaHCO_3$ +0.02 cc. 1 *M* Na_2CO_3 +4.8 cc. H_2O	solid
(3)	5 cc. 2% gel. +0.16 cc. 1 *M* $NaHCO_3$ +0.04 cc. 1 *M* Na_2CO_3 +4.8 cc. H_2O	solid
(4)	5 cc. 2% gel. +0.14 cc. 1 M $NaHCO_3$ +0.06 cc. 1 *M* Na_2CO_3 +4 8 cc H_2O	solid
(5)	5 cc 2% gel +0 12 cc 1 *M* $NaHCO_3$ +0 08 cc 1 *M* Na_2CO_3 +4 8 cc H_2O	solid
(6)	5 cc 2% gel. +0.10 cc. 1 *M* $NaHCO_3$ +0.10 cc. 1 *M* Na_2CO_3 +4.8 cc. H_2O	solid
(7)	5 cc. 2% gel. +0.08 cc. 1 *M* $NaHCO_3$ +0.12 cc. 1 *M* Na_2CO_3 +4.8 cc. H_2O	solid
(8)	5 cc. 2% gel. +0.06 cc. 1 *M* $NaHCO_3$ +0.14 cc. 1 *M* Na_2CO_3 +4.8 cc. H_2O	solid
(9)	5 cc. 2% gel. +0.04 cc. 1 *M* $NaHCO_3$ +0.16 cc. 1 *M* Na_2CO_3 +4.8 cc. H_2O	solid
(10)	5 cc. 2% gel. +0.02 cc. 1 *M* $NaHCO_3$ +0.18 cc. 1 *M* Na_2CO_3 +4.8 cc. H_2O	solid
(11)	5 cc. 2% gel. +0.20 cc. 1 *M* Na_2CO_3 +4.80 cc. H_2O	solid
(12)	5 cc. 2% gel. +0.18 cc. 1 *M* Na_2CO_3 +0.02 cc. 1 *N* NaOH +4.8 cc. H_2O	solid
(13)	5 cc. 2% gel. +0.16 cc. 1 *M* Na_2CO_3 +0.04 cc. 1 *N* NaOH +4.8 cc. H_2O	solid
(14)	5 cc. 2% gel. +0.14 cc. 1 *M* Na_2CO_3 +0.06 cc. 1 *N* NaOH +4.8 cc. H_2O	semi-solid
(15)	5 cc. 2% gel. +0.12 cc. 1 *M* Na_2CO_3 +0.08 cc. 1 *N* NaOH +4.8 cc. H_2O	semi-solid
(16)	5 cc. 2% gel. +0.10 cc. 1 *M* Na_2CO_3 +0.10 cc. 1 *N* NaOH +4.8 cc. H_2O	liquid
(17)	5 cc. 2% gel. +0.08 cc. 1 *M* Na_2CO_3 +0.12 cc. 1 *N* NaOH +4.8 cc. H_2O	liquid
(18)	5 cc. 2% gel. +0.06 cc. 1 *M* Na_2CO_3 +0.14 cc. 1 *N* NaOH +4.8 cc. H_2O	liquid
(19)	5 cc. 2% gel. +0.04 cc. 1 *M* Na_2CO_3 +0.16 cc. 1 *N* NaOH +4.8 cc. H_2O	liquid
(20)	5 cc. 2% gel. +0.02 cc. 1 *M* Na_2CO_3 +0.18 cc. 1 *N* NaOH +4.8 cc. H_2O	liquid
(21)	5 cc. 2% gel. +0.20 cc. 1 *N* NaOH +4.80 cc. H_2O	liquid

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should be found to gel upon the addition of acid, for the addition of acid increases hydration. As our previous experiments have shown and as indicated by those detailed in this paper, opposite conditions obtain, for the addition of acid or of alkali will make an already solid gelatin gel become not stiffer but more liquid. We seem to be justified in the assumption that gelatin is a chemical substance capable of existing in different degrees of association or polymerization depending upon the temperature and upon other changes in its environment, like the presence of acids or of alkalies. The degree of association and hence the size of the particles of which the gelatin is composed may be greatly varied. At the higher temperatures and under the influences of acids and alkalies, for example, the particles become smaller, while under reverse conditions they become larger. With these changes in size, they change their physicochemical properties so that under the former circumstances they are liquid and clear, while under the latter they become solid and opalescent. The particles seem capable of absorbing most water (becoming most heavily hydrated) when they have a medium diameter. Neutral gelatin in which the particles are large, therefore absorbs some water, which absorption on the addition of acid (which multiplies the particles and makes them smaller) is increased. On further addition of acid, however, the particles decrease in size to beyond that optimal for swelling. In this region the mixture as a whole begins to liquefy and shortly thereafter to show prominent evidences of "going into solution."

These experiments seem to us to help to explain the successive changes observable in living cells when these are subjected to a direct acid intoxication or to an indirect acid intoxication through so-called "injury" by mechanical, thermal or chemical means. After injury, tissues pass through a primary period of swelling into a second one of softening[1] with evidences of protoplasmic liquefaction and solution. In the terms of colloid chemistry, we would say that under the influences of the acids and similarly acting substances brought into play through the injury, the tissues first swell; as their acid content rises, protein dissociation becomes more prominent and betrays itself by a greater tendency of the tissues to liquefy and since hydration is now less, the tissues soften and "dissolve" in the media bathing them (be this sea water, blood, lymph or urine).

These experiments also bear upon the problem of digestion and that special phase of it known as autolysis. The first changes observable in these reactions consist of swelling, followed by a softening and dissolution of the proteins acted upon. Acids and alkalies have long been

[1] For a discussion of the "solidity" of living tissues as dependent upon their emulsion character and for the "softening" of such tissues consequent upon the "breaking" of the emulsion see Martin H. Fischer and Marion O. Hooker, "Fats and Fatty Degeneration," New York, 76 (1917).

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known to favor these initial steps in proteolysis, while all salts, including such "buffer" salts as phosphates or citrates, have been known to inhibit them. Their action has usually been laid to an effect upon the enzymes themselves. As has been pointed out before, acids, alkalies and salts produce at least as large and probably their greatest effects upon the proteins undergoing digestion. The important theoretical and practical bearings of such considerations upon laboratory practice and the everyday problems of the hanging of meat, its preservation by salting, the prevention of putrefaction, etc., are self-evident.

These experiments emphasize again the necessity of interpreting in the simpler language of colloid-chemistry the mass of experimental material now collected by the biologists under the heading of "permeability" studies. It means little to say that under the influence of acids or of substances which in living cells produce acid effects (like the anesthetics) the "permeability" of the "plasma" membranes surrounding cells is increased so that albumin gets out or salts get in. Not only are plasma membranes figments of the imagination, but nothing is gained by heaping "permeability" properties upon them. "Permeability" is a physiological concept which itself needs to be explained. The proteins throughout a cell (not only in its hypothetical overcoat) can under the influence of acids, for example, be made to absorb water, to absorb salt,[1] to soften and to give off albumin. And as all these effects may be observed in simple proteins where their exact nature is more accessible to quantitative study and further analysis than in the case of our complex living cells, it would look like a better conservation of mental energy to concentrate further study upon the colloid-chemical principles here to the front than to continue indefinitely the mere restatement of biological problems in the terms of biology itself.

CINCINNATI, OHIO.

[CONTRIBUTION FROM THE HYGIENIC LABORATORY, U. S. PUBLIC HEALTH SERVICE.]

THE UTILIZATION OF THE ADSORPTIVE POWER OF FULLER'S EARTH FOR CHEMICAL SEPARATIONS.

BY ATHERTON SEIDELL.

Received November 12, 1917.

The utilization of fuller's earth for chemical separations (other than decolorizations) has, in recent years, found at least two practical applications. The first of these is its use in connection with the isolation of alkaloids[2] from plants or their extracts and the second forms an important

[1] Martin H. Fischer, *J. Am. Med. Assoc.*, 64, 325 (1915).

[2] Sigmund Waldbott, "Precipitating Alkaloids by Lloyd's Reagent—Preliminary Note," THIS JOURNAL, 35, 837 (1913).

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step in the more or less complete separation of "vitamines"[1] from the complex mixtures in which they occur. In neither case has detailed information been given in regard to the particular conditions under which the adsorptive power can be utilized to best advantage. It was simply learned by empirical experiments, that if a sufficient amount of a particular variety of fuller's earth was shaken for a short time with a neutral or slightly acid solution containing an alkaloid or "vitamine," the filtrate from the mixture would fail to give a positive test for the one or the other as the case might be. No data are available on such matters as the effect on the adsorptive process of time, agitation, dilution, reaction, presence of other dissolved substances, variations in the proportion of earth used, etc.

The results of comparative tests of the adsorptive powers of fuller's earths from various sources have been published,[2] but little information has been given in regard to the technic of the methods employed. These experiments showed that of all the samples tested, a particular variety of earth designated as "Lloyd's reagent" exerted the highest adsorptive power. Information in regard to the source of this earth and particulars concerning its preparation for use are not given. Although there was no reason to question the correctness of the results of the comparative tests referred to above, it was believed that additional data along this line, obtained by a more clearly defined method, would be of interest.

Relative Adsorptive Power of Various Fuller's Earths.—In the case of most of the previous experiments made in this connection, the basis for expressing the results has been the quantity of fuller's earth required to adsorb unit quantity of alkaloid. Since, however, it is a question of comparing the various samples of earth with each other, it was believed that a more direct estimate would be that based on the amount of alkaloid adsorbed by unit quantity of the various samples. This basis has, therefore, been adopted for the results here given.

Preliminary experiments showed that the adsorption process is not instantaneous and therefore that sufficient time of contact of solution with the solid must be allowed. Furthermore, since the bulk of the earth rapidly subsides on standing, it is necessary that continual agitation be employed.

Since the main object was a comparison of the fuller's earth samples with each other, the particular alkaloid used did not appear to be of consequence. Quinine bisulfate ($C_{20}H_{24}N_2O_2H_2SO_4.7H_2O$) was, therefore, arbitrarily selected. In addition to the results obtained with quinine bisulfate, it was considered of interest to secure a series of comparative figures for another compound of different character. Methylene blue

[1] A. Seidell, *Pub. Health Reports*, 31, 364 (1916).

[2] Bernard Fantus, *J. Am. Med. Assoc.*, 64, 1838 (1915); J. Uri Lloyd, *J. Am. Pharm. Assoc.*, 5, 381, 490 (1916).

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(tetramethylthionine chloride, $C_{16}H_{18}N_3ClS.3H_2O$) was selected for this purpose. Two series of results have, therefore, been obtained using exactly the same procedure in both cases, one showing the adsorption coefficients obtained with quinine bisulfate and the other with methylene blue.

The samples of fuller's earth were obtained from the several sources mentioned in Table I. Those from Chas. L. Parsons of the Bureau of Mines were collected by him some years ago for comparative cottonseed oil decolorization tests and additional information in regard to these is given in Parsons' publication.[1] The samples[2] as received were for the most part in the form of lumps, but in each case were ground to pass a No. 60 or finer mesh screen and thoroughly mixed before being used.

The method adopted for the tests was as follows: One gram portions of the fuller's earth sample and about 10 cc. of water were placed in a series of test tubes of 60 cc. or more capacity and, after thoroughly mixing, accurately measured volumes of 1.0% quinine bisulfate solution or 0.5% methylene blue solution were added. Rubber stoppers were inserted and the tubes attached to a frame which was kept in rotation for one-half hour. The contents of the tubes were then quickly filtered into other test tubes and the filtrates, in the case of the quinine bisulfate solutions, treated with about three drops of Mayer's alkaloidal reagent. Tests with a given sample of fuller's earth were repeated as above with increasing amounts of quinine bisulfate, until a quantity was found that yielded a filtrate in which a just perceptible clouding resulted on addition of the Mayer reagent. In the case of the methylene blue solutions the test was repeated until a just perceptible blue color could be detected in the filtrate. From the volumes of solutions of quinine bisulfate and methylene blue corresponding to these end points, the values in terms of grams of each compound adsorbed per 100 g. of the fuller's earth sample were calculated and the results given in Table I.

The samples are arranged in this table according to descending amounts of quinine bisulfate adsorbed. It will be noted that, in general, there is a parallelism between the amounts of alkaloid and of methylene blue adsorbed. Also that with two or three exceptions the figure for methylene blue is somewhat higher than that for quinine bisulfate.

The samples of bentonite show particularly high adsorptive coefficients and would, therefore, be expected to be especially useful as absorbents. It is to be mentioned, however, that, from the manipulative standpoint, they have the practical disadvantage of taking up very large quantities of water to form gelatinous masses from which the aqueous solution cannot be completely separated by filtration or centrifugation. Although this

[1] "FULLER'S EARTH," Bureau of Mines, *Bull.* 71, 1913.

[2] The author desires to acknowledge his indebtedness to all those who have contributed samples for these tests.

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property of bentonite no doubt makes it of great value for other purposes, it renders it less suitable for quantitative chemical separations.

TABLE I.—ADSORPTION COEFFICIENTS OF FULLER'S EARTHS AND OTHER CLAYS EXPRESSED IN TERMS OF G. OF QUININE BISULFATE AND OF METHYLENE BLUE ADSORBED PER 100 G. OF EACH SAMPLE.

(Volume of solution, about 30 cc. in each case; time of contact at constant agitation, one-half hour.)

Description of sample.	Supplied by.	Adsorption coefficients. Quinine bisulfate.	Adsorption coefficients. Methylene blue.
Bentonite, Newcastle, Wyo.	F. W. Mondell	20.0	18.0
Bentonite, Wyoming	National Museum	18.0	27.8
Fuller's earth, Utah	National Museum	17.5	18.7
Bentonite, Halleck, Cal.	R. B. Flenniken	16.0	18.0
Fuller's earth, Surrey, England	Eimer & Amend	16.0	16.0
"Lloyd's reagent" (white)	J. U. Lloyd	15.5	23.8
"Lloyd's reagent"	J. U. Lloyd	15.5	17.8
Fuller's earth (red), Buckingham, Eng.	National Museum	15.0	14.8
Fuller's earth (gray), Buckingham, Eng.	National Museum	15.0	13.8
Fuller's earth, English	Chas. L. Parsons	15.0	13.5
Fuller's earth, Custer Co., S. D.	National Museum	12.5	15.0
Fuller's earth	A. H. Thomas & Co.	12.0	14.8
Fuller's earth	Shoemaker & Busch	12.0	14.8
Bentonite, Utah	National Museum	12.0	22.5
Fuller's earth, Sommerville, Tex.	H. C. Gore	8.0	10.0
Fuller's earth, Carlton, Ga.	Chas. L. Parsons	7.8	9.9
Dark clay (prob. Bentonite), Halleck, Cal.	R. B. Flenniken	7.0	9.0
Fuller's earth (old sample), Carlton, Ga.	Chas. L. Parsons	6.5	8.0
Fuller's earth, Fitzpatrick, Ga.	Chas. L. Parsons	6.0	9.8
Fuller's earth, Vacaville, Cal.	Chas. L. Parsons	5.0	8.5
Fuller's earth, Moultrie, Ga.	Chas. L. Parsons	4.0	6.0
Fuller's earth, Attapulgus, Ga.	Chas. L. Parsons	3.5	5.7
Fuller's earth, Sumpter, S. C.	Chas. L. Parsons	3.5	5.4
Fuller's earth	Scientific Materials Co.	3.5	5.8
Fuller's earth, Benton, Ark.	H. C. Gore	2.5	3.0
Clay No. 1, Kingsbury	Chas. L. Parsons	1.5	2.4
Fuller's earth (ignited)	Texas Oil Co.	1.5	3.4
Fuller's earth, Midway, Fla.	Chas. L. Parsons	1.3	2.9
Fuller's earth, Ellenton, Fla.	Chas. L. Parsons	1.3	3.3
Fuller's earth, Ellenton, Fla.	Chas. L. Parsons	1.2	3.7
Kieselguhr	A. H. Thomas & Co.	1.2	1.8
Fuller's earth, Ft. Payne, Ala.	Chas. L. Parsons	1.0	1.7
Fuller's earth, Andalusia, Ala.	Chas. L. Parsons	0.4	1.2
Fuller's earth, Lancaster, Mass.	Chas. L. Parsons	0.3	0.7
Halloysite, Utah	National Museum	0.3	1.0
Fuller's earth(?)	Bausch & Lomb	0.2	0.2

In regard to the results obtained with the fuller's earth samples, it is seen that all of those from England have very nearly the same coefficient for quinine bisulfate and this figure is very close to that found for "Lloyd's reagent." The American samples, with the exception of the one from

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Utah for which further details in regard to its origin could not be obtained, have distinctly lower adsorption coefficients. In the case of some of these it is possible that by proper treatment for removal of inactive portions, products of higher coefficients could be prepared. The English earth is, however, readily obtainable and evidently of very uniform adsorptive power since various samples of it, which have so far been examined, show values in close agreement with those recorded in the table.

Effect of Time on Rate of Adsorption.—As already mentioned, preliminary experiments showed that the process of adsorption is not instantaneous and consequently that sufficient time must be allowed for attainment of equilibrium. The following experiments were, therefore, made to obtain data on this point:

The results of the first experiment are shown in Table II and Chart I. In this case, 10 cc. portions of a 1 per cent. quinine bisulfate solution and different amounts of English fuller's earth mixed with about 20 cc. of water, were shaken at intervals for the periods shown, and the mixtures quickly filtered. The filtrates were tested with Mayers' reagent and the completeness of the adsorption judged by the extent of clouding which resulted. A summary is given in the lower part of the table showing the

TABLE II.—EFFECT OF TIME ON ADSORPTION OF QUININE BISULFATE BY ENGLISH FULLER'S EARTH (E. & A.).

Composition of mixture in grams.			Time.	
Quinine bisulfate.	Fuller's earth.	H_2O.	of contact, minutes.	Appearance of filtrate on addition of Mayer's reagent.
0.1	0.7	30	5	Immediate clouding
0.1	0.7	30	10	Clouding less than preceding
0.1	0.7	30	15	Very faint clouding
0.1	0.675	30	15	Faint clouding
0.1	0.675	30	20	Very faint clouding
0.1	0.633	30	40	Faint clouding
0.1	0.625	30	60	Clear
0.1	0.600	30	60	Cloudy
0.1	0.610	30	80	Very faint clouding
0.1	0.600	30	120	Cloudy
0.1	0.600	30	20 hours	Clear
0.1	0.575	30	20 hours	Very faint clouding
0.1	0.550	30	20 hours	Cloudy

SUMMARY OF THE ABOVE.

Time.	G. fuller's earth to just adsorb 0.1 g. quinine bisulfate.	Calc. g. quinine bisulfate just adsorbed per 100 g. fuller's earth.
15 minutes	0.7	14.3
20 minutes	0.675	14.8
40 minutes	0.633	15.8
60 minutes	0.625 (slightly high)	16.0
80 minutes	0.61	16.5
120 minutes	0.600 (slightly low)	16.7
20 hours	0.575	17.4

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amounts of fuller's earth required, on the basis of the qualitative test for unadsorbed alkaloid, to just completely adsorb 0.1 g. of quinine bisulfate in the several periods of time. The reciprocals of these values (× 100) showing the grams of quinine bisulfate which would be just adsorbed by 100 g. of fuller's earth in the time stated, are also given. These latter values, together with the results obtained with methylene blue, are plotted in Chart I.

The experiments with methylene blue were made as follows: A number of tubes were prepared containing the same ratio of methylene blue to fuller's earth in each. These were rotated for different lengths of time and the unadsorbed methylene blue estimated in the filtrate from each mixture by a colorimetric comparison. The quantities thus found were deducted from the methylene blue originally present and the amount adsorbed thus calculated by difference. Results are given in Table III for two different ratios of methylene blue to fuller's earth. For the purpose of comparing with the preceding experiment, the figures are also calculated to grams of methylene blue adsorbed by 100 g. of fuller's earth. These values, together with the corresponding results obtained with quinine bisulfate are plotted in Chart I. They show strikingly, that the rate of adsorption is very greatly accelerated by increase of excess of material to be adsorbed.

TABLE III.—EFFECT OF TIME ON ADSORPTION OF METHYLENE BLUE BY ENGLISH FULLER'S EARTH (E. & A.).

Series.	Composition of original mixture in g.			Time of constant agitation. (Min.).	G. methylene blue adsorbed.	
	Fuller's earth.	Methylene blue.	H_2O.		Per 0.25 g. fuller's earth.	Per 100 g. fuller's earth.
I.....	0.25	0.045	30	10	0.0388	15.52
	0.25	0.045	30	30	0.0436	17.44
	0.25	0.045	30	60	0.0446	17.84
	0.25	0.045	30	120	0.0449	17.96
II.....	0.25	0.075	30	10	0.0450	18.00
	0.25	0.075	30	30	0.0557	22.28
	0.25	0.075	30	60	0.0564	22.56
	0.25	0.075	30	120	0.0569	22.76

It is to be noted that in the case of the methylene blue experiment, a fairly large excess was used in one case and a smaller but considerable excess in the other, whereas with the quinine bisulfate no greater excess was present than sufficient to permit the detection of the end point. The curves given in Chart I show that the rate of adsorption is proportional to the excess of material to be adsorbed. The question of the selection of the proper time to be allowed for adsorption in practical work is, therefore, complicated by this factor of influence of excess of adsorbable material present. The curve for quinine bisulfate represents exactly the conditions selected for making the comparisons of the various fuller's earth samples as

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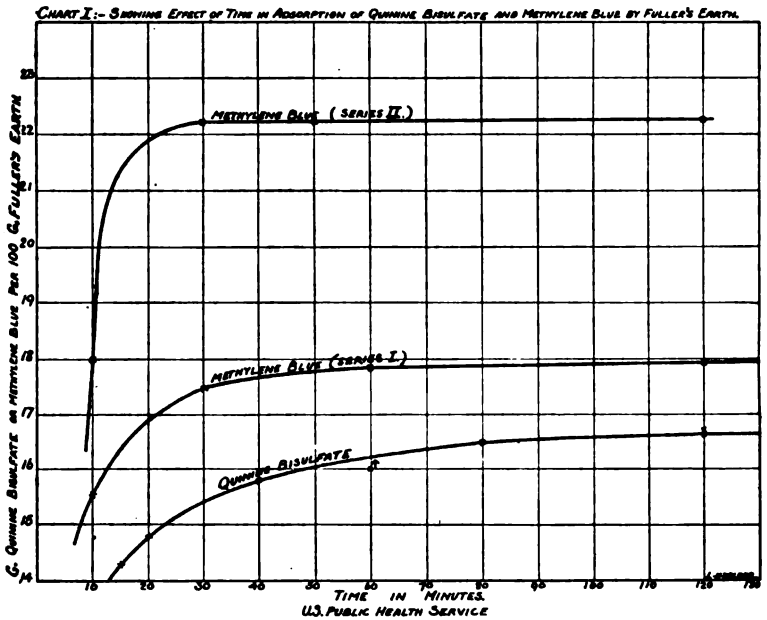
shown in Table I; that is, the end point representing no excess of material to be adsorbed. This curve rises most gradually of all and no relatively short time period can be selected from it as having a particular advantage over another. The one-half hour period which was arbitrarily selected



for the comparative tests already described has, no doubt, given as trustworthy results as would have been obtained by a longer period. The curve here shown, however, emphasizes strongly the necessity for a rigid control of the time factor in comparing various samples of fuller's earth.

Effect of Excess of Methylene Blue and of Quinine Bisulfate upon Their Adsorption by Fuller's Earth.—Since, as shown in the preceding section, the rapidity of the adsorption is greatly increased by excess of methylene blue, it appeared of interest to ascertain the effect of this factor on the quantity of methylene blue and of quinine bisulfate adsorbed.

In the case of this and all other experiments with methylene blue, a sample was used which contained 0.87% ash and in other respects conformed to the pharmacopoeial requirements for tetramethylthionine chloride ($C_{16}H_{18}N_3ClS.3H_2O$). Gradually increasing amounts of a solution of this product were added to accurately weighed portions of English fuller's earth (E. & A.), to yield mixtures of the compositions shown in Table IV, and these constantly agitated for one-half hour. They were then quickly centrifugated and aliquot portions of the clear supernatant solutions removed for determination of the unadsorbed methylene blue

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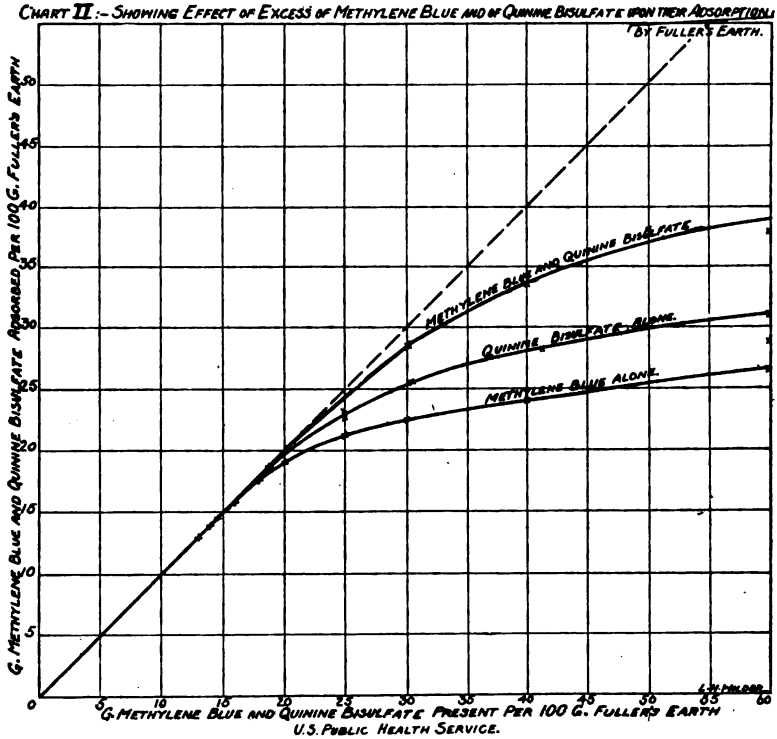
by a colorimetric comparison. Centrifugation was employed rather than filtration since it was found that considerable color is removed from the solution by the paper filters. The results of this experiment are given in Table IV and shown graphically in Chart II.

TABLE IV.—EFFECT OF EXCESS OF METHYLENE BLUE UPON ITS ADSORPTION BY FULLER'S EARTH.

(Mixtures constantly agitated for one-half hour.)

Composition of original mixture in g.			G. methylene blue calculated to 100 g. fuller's earth.		
Fuller's earth.	Methylene blue.	H_2O.	Originally present.	Unadsorbed (det. colorimetrically).	Adsorbed. (calc. by diff.).
0.5	0.065	30	13.0	0.013	12.987
0.5	0.070	30	14.0	0.020	13.980
0.5	0 0725	30	14.5	0.022	14.478
0.5	0.080	30	16.0	0.055	15.945
0.5	0.090	30	18.0	0.270	17.730
0.5	0.100	30	20.0	0.915	19.085
0.5	0.125	30	25.0	3.75	21.250
0.5	0.150	60	30.0	7.73	22.280
0.5	0.200	60	40.0	16.00	24.000
0.5	0.300	60	60.0	33.60	26.400

CHART II:—SHOWING EFFECT OF EXCESS OF METHYLENE BLUE AND OF QUININE BISULFATE UPON THEIR ADSORPTION BY FULLER'S EARTH.



It is seen that the amount of methylene blue adsorbed continues to increase with each additional increment of coloring matter in solution but

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the rate of increase gradually diminishes. There appears to be no definite limit for the total amount of the compound which can be adsorbed per unit of fuller's earth.

Considerable difficulty has been experienced in preparing a chart which would exhibit clearly the change in the adsorption due to increasing excess of adsorbable color. It is evident that up to a certain point all of the methylene blue is completely adsorbed. There is, however, no sharp break at this point. The amount of color adsorbed from this point on represents a gradually diminishing fraction of that present. The unadsorbed fraction, therefore, begins as a mere trace at a certain point which obviously cannot be accurately determined, and increases almost imperceptibly at first, and then more and more rapidly. On this account, it follows that, in attempting to ascertain the adsorptive capacity of a given sample of fuller's earth by determination of the maximum amount of methylene blue which will be *just* completely adsorbed by it within a definite time, the end point of the test comes at exactly that part of the curve where very small differences in the estimated amount of unadsorbed color correspond to relatively large differences in amount adsorbed. Furthermore, errors due to filtering through paper, to which attention has already been called, are accentuated at this portion of the curve. The magnitude of the error due to filter paper is indicated by comparing the adsorption coefficient given in Table I for the sample of fuller's earth used in the present experiment (Surrey, England, E. & A.) with the coefficient which is derived from Table IV. In the one case, filtration through paper was used and the value was found to be 16 g. methylene blue per 100 g. of the sample, while in the other, in which removal of the solid was effected by centrifugation, it would be placed at slightly less than 13 g. For these and other reasons, it is apparent that the values given in Table I for the adsorption coefficients of various samples of fuller's earth can be considered of interest only as showing the relative position of the several samples in the series. Even the very great care which was exercised to maintain uniform conditions could not be expected to overcome the limitations of the test described above.

In order to gain some information in regard to how firmly the methylene blue is combined with the fuller's earth when the combination has been made in the presence of the very considerable excesses of methylene blue shown in Table IV, the residues left in the centrifuge tubes after decantation of the clear liquids were, without washing, stirred up with 30 cc. portions of water. The mixtures were constantly agitated for one-half hour and then allowed to stand two days. The methylene blue in the supernatant liquids was then estimated colorimetrically as before. The results calculated to the basis of g. per 100 g. fuller's earth are, respectively, 0.0004, 0.0005, 0.0005, 0.0012, 0.0050, 0.0145, 0.050, 0.100, 0.342 and 0.732.

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These amounts are no greater than could be accounted for by methylene blue solution mechanically held by the residues in the centrifuge tubes. It, therefore, seems probable that methylene blue adsorbed by fuller's earth in presence of a large excess of the color is held just as firmly as that taken up from less concentrated solutions.

The experiment with quinine bisulfate was made as described above for methylene blue. The mixtures were rotated for one-half hour, the suspended solid thrown down by centrifugation and the unadsorbed quinine bisulfate remaining in the clear supernatant solution titrated with 0.02 *N* sodium hydroxide, using phenolphthalein as indicator. The results are given in Table V and plotted in Chart II. The curve lies somewhat above that for methylene blue but is similar to it.

TABLE V.—EFFECT OF EXCESS OF QUININE BISULFATE UPON ITS ADSORPTION BY FULLER'S EARTH.

(Mixtures constantly agitated for one-half hour.)

	Composition of original mixture in g.			G. quinine bisulfate calculated to 100 g. fuller's earth.		
Series.	Fuller's earth.	Quinine bisulfate.	H_2O.	Originally present.	Unadsorbed (det. volumetrically).	Adsorbed (calc. by diff.).
I.....	0.5	0.093	30	18.6	Trace	18.6
I.....	0.5	0.124	30	24.8	1.6	23.2
I.....	0.5	0.206	30	41.24	12.94	28.3
I.....	0.5	0.309	30	60.17	30.90	30.9
II.....	1.0	0.185	40	18.5	Trace	18.5
II.....	1.0	0.247	40	24.7	2.0	22.7
II.....	1.0	0.309	40	30.9	5.1	25.8
II.....	0.5	0.309	40	60.18	32.4	27.8

Evidence that the Free Base Only Is Adsorbed when Solutions of Methylene Blue and Quinine Bisulfate are Placed in Contact with Fuller's Earth.—In the case of the second series of experiments recorded in Table V an aliquot of each supernatant solution was evaporated to dryness on the steam bath. It was found that the residues thus obtained weighed more than the quinine bisulfate calculated from the volumetric determinations. In the case of the first mixture of this second series in which only a trace of unadsorbed quinine remained in the aqueous solution, it was found that the residue obtained on evaporation consisted of nearly pure calcium sulfate. The amount of sulfate radical present in the residue corresponded almost exactly with that calculated from the amount of quinine adsorbed. It is, therefore, evident that when quinine bisulfate is shaken with fuller's earth, the quinine only unites with the earth and the acid is liberated.

A similar experiment was made with methylene blue and it was ascertained that here also only the free base is adsorbed and a chloride remains behind in the aqueous solution. The analytical results were obtained on a solution (Table IV, first mixture) containing only a trace of unadsorbed

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methylene blue and showed that the amount of chloride remaining in the aqueous solution agreed closely with that originally in combination with methylene blue. The aqueous solution also contained calcium, thus indicating that also in this case the liberated acid is neutralized by the calcium of the fuller's earth. A confirmatory test of the absence of chloride in the methylene blue adsorbed to fuller's earth was made by igniting a portion of the dried product in the presence of alkali carbonate, extracting with water, acidifying and adding silver nitrate. A very faint opalescence showed that not more than a trace of chloride was present. Although the above experiments show that only the free base unites with the fuller's earth in each case, the figures in all the tables are, for convenience, given in terms of the weight of the original compound adsorbed and remaining unadsorbed.

The Simultaneous Adsorption of Quinine Bisulfate and Methylene Blue by Fuller's Earth.—Since the preceding experiments have shown the amounts of quinine bisulfate and of methylene blue which are adsorbed when each is present separately, it appeared of interest to ascertain how much of each is adsorbed when both are simultaneously present in equal amounts, and thus to determine whether fuller's earth shows any selective action in the adsorption of one or the other of these two compounds.

TABLE VI.—SIMULTANEOUS ADSORPTION OF METHYLENE BLUE AND QUININE BISULFATE BY FULLER'S EARTH.

(Mixtures constantly agitated for one-half hour.)

Composition of original mixture in g.				G. adsorbed per 1.0 g. fuller's earth.		
Fuller's earth.	Methylene blue.	Quinine bisulfate.	H_2O.	Methylene blue.	Quinine bisulfate.	Total.
1.0	0.05	0.05	100	0.05	0.05	0.10
1.0	0.10	0.10	100	0.10	0.10	0.20
1.0	0.15	0.15	100	0.149	0.136	0.285
1:0	0.20	0.20	100	0.173	0.162	0.335
1.0	0.25	0.25	100	0.182	0.197	0.379
1.0	0.30	0.30	100	0.186	0.192	0.378

With the above object in view, mixtures of the compositions shown in Table VI were prepared and rotated for one-half hour as in the previous experiments. The solid was thrown down by centrifugation and the decanted clear liquids used for determination of the amounts of the two compounds remaining unadsorbed. An aliquot portion in each case was first used for the estimation of methylene blue by a colorimetric comparison. Another aliquot portion was evaporated to dryness on the steam bath and the residue weighed. As pointed out in the preceding section, this residue contains not only the unadsorbed quinine bisulfate and methylene blue but also calcium sulfate and chloride equivalent, respectively, to the amounts of each free base adsorbed. The amount of methylene blue in the evaporated residues was, as mentioned above, ascertained from the

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colorimetric comparison of the separate portion of the solution. No method of isolating the quinine bisulfate from the mixture or of estimating it in the presence of the methylene blue has, so far, been devised. Immiscible solvents fail to effect a separation in either acid or alkaline solution. It was therefore necessary to rely upon an indirect procedure for estimating the amount of this constituent which remained unadsorbed. This was done, in the present case, in two ways, first by treating each residue with absolute alcohol and filtering through a weighed Gooch funnel. From the weight of calcium sulfate thus separated, the adsorbed quinine was calculated directly. Secondly, the sum of the determined methylene blue and calcium sulfate and of the estimated calcium chloride (from methylene blue adsorbed) was deducted from the total weight of the residue and the difference assumed to be quinine bisulfate. The values for unadsorbed quinine bisulfate obtained by these two indirect methods agree fairly satisfactorily and from them the results shown in Table VI have been calculated. It is seen that nearly equal amounts of the two substances are adsorbed in each case. The sum of the two is considerably greater than the amount of either adsorbed separately.

The figures representing these totals (multiplied by 100) have been plotted in Chart II. They illustrate the magnitude of this increase of adsorptive capacity resulting from the simultaneous presence of the two compounds over that found for either one separately. The results also indicate that fuller's earth shows no marked preference for either compound when approximately equal amounts of the two are simultaneously present in solution.

The Successive Adsorption of Methylene Blue and Quinine Bisulfate by a Single Portion of Fuller's Earth.—These experiments were made by first shaking given solutions of one of the compounds with fuller's earth and after removing the solid by centrifugation, adding solutions of known amounts of the other compound and proceding just as before. The supernatant solutions were analyzed in both cases and the amounts of each compound uniting with fuller's earth, or displaced from it as the case might be, determined by difference. The results of these experiments are given in Tables VII and VIII. From these it is seen that, when fuller's earth containing adsorbed methylene blue is shaken with quinine bisulfate solutions, practically none of the methylene blue is displaced from its combination with fuller's earth and the amounts of quinine bisulfate adsorbed decrease with the increasing amounts of methylene blue united to the fuller's earth. On the other hand, when the procedure is reversed, methylene blue is not only adsorbed in proportion to the increasing amount of it present, but it even displaces a considerable part of the quinine bisulfate from its combination with the fuller's earth. In this latter case the total amount of the two compounds finally present agrees well with the totals

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found in the experiment described in the preceding section and plotted in Chart II, showing the amounts of the two compounds simultaneously adsorbed from solution. On the basis of the present results it appears that, under the conditions here described, fuller's earth exhibits a stronger affinity for methylene blue than for quinine bisulfate. This difference is, however, certainly not of sufficient magnitude to be utilized in separating one of the compounds from the other.

TABLE VII.—ADSORPTION OF QUININE BISULFATE BY FULLER'S EARTH CONTAINING ADSORBED METHYLENE BLUE.

G. original fuller's earth.	G. adsorbed methylene blue present.	G. quinine bisulfate added as 1% solution.	Volume of mixture. Cc.	After ½ hr. rotation. G. displaced methylene blue.	After ½ hr. rotation. G. adsorbed quinine bisulfate.	Total g. methylene blue + quinine bisulfate adsorbed.
1.0	0.10	0.10	100	0.000	0.100	0.20
1.0	0.15	0.15	100	0.000075	0.104	0.254
1.0	0.20	0.25	100	0.00016	0.076	0.276
1.0	0.21	0.40	100	0.000175	0.072	0.282

TABLE VIII.—ADSORPTION OF METHYLENE BLUE BY FULLER'S EARTH CONTAINING ADSORBED QUININE BISULFATE.

G. original fuller's earth.	G. adsorbed quinine bisulfate present.	G. methylene blue added as 0.5 % solution.	Volume of mixture. Cc.	After ½ hr. rotation. G. displaced quinine bisulfate.[1]	After ½ hr. rotation. G. adsorbed methylene blue.	Total g. methylene blue + quinine bisulfate adsorbed.
1.0	0.18	0.09	80	0.017	0.090	0.253
1.0	0.232	0.12	80	0.023	0.1198	0.329
1.0	0.283	0.20	80	0.059	0.1643	0.388
1.0	0.309	0.30	80	0.088	0.1950	0.416

Effect of Dilution with Water on the Adsorption of Quinine Bisulfate by Fuller's Earth.—This experiment was made by rotating mixtures of the compositions shown in Table IX for the usual one-half hour period, filtering quickly through Gooch crucibles and titrating the unadsorbed quinine bisulfate in the filtrates with 0.02 *N* sodium hydroxide, using phenolphthalein as indicator. The volumes of the solutions varied from 15 cc. to 90 cc. in the case where 0.15 g. quinine bisulfate per 1.0 g. of fuller's earth had been used and from 30 to 90 cc. where 0.3 g. of the alkaloidal salt was present. Control titrations showed that the end point was affected very slightly by increase of dilution and a correction was applied for this. It will be observed that at the lower ratio of alkaloid to fuller's earth the effect of increasing the volume of water is practically negligible. At the higher ratio it is still not of sufficient magnitude to be of consequence in the practical utilization of fuller's earth for chemical separations. It appears that, if sufficient fuller's earth is present to adsorb all the alkaloid in a small volume of solution, a very considerable dilution with water does not appreciably diminish the adsorbing power of the

[1] Estimated indirectly from total solids determinations.

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earth. When insufficient fuller's earth is used to completely adsorb all of the alkaloid present, an increase in dilution appreciably reduced the proportion of alkaloid which is adsorbed. To insure complete adsorption at any dilution, it is, therefore, only necessary to use that amount of fuller's earth which has been found at low dilutions to be sufficient to adsorb all the material without leaving any unadsorbed.

TABLE IX.—SHOWING THE EFFECT OF DILUTION WITH WATER UPON THE ADSORPTION OF QUININE BISULFATE BY FULLER'S EARTH.

(Mixtures rotated one-half hour and filtered through Gooch crucible.)

G. English fuller's earth.	1% quinine bisulfate solution. Cc.	H_2O added. Cc.	G. quinine bisulfate adsorbed per 1.0 g. fuller's earth.
1.0	15	0	0.149
1.0	15	15	0.148
1.0	15	75	0.147
1.0	30	0	0.263
1.0	30	30	0.252
1.0	30	60	0.250

Effect of Acidity on the Adsorption of Quinine Bisulfate by Fuller's Earth.—As pointed out in a previous section of this paper, when either quinine bisulfate or methylene blue is shaken with fuller's earth only the base in each case is adsorbed and the liberated acid unites with calcium from the earth and remains in the aqueous solution. It, therefore, appeared of interest to ascertain the effect of increasing acidity upon this reaction.

TABLE X.—EFFECT OF HYDROCHLORIC ACID ON THE ADSORPTION OF QUININE BISULFATE BY FULLER'S EARTH.

(Each mixture rotated one-half hour and the solid removed by centrifugation.)

G. English fuller's earth.	Quinine bisulfate. G.	Volume mixture. Cc.	Normality HCl.	G. quinine bisulfate adsorbed per 1.0 g. fuller's earth.
1.0	0.15	50	0.000	0.148
1.0	0.15	50	0.004	0.148
1.0	0.15	50	0.020	0.145
1.0	0.15	50	0.10	0.143
1.0	0.15	50	0.40	0.135
1.0	0.30	50	0.000	0.256
1.0	0.30	50	0.004	0.232
1.0	0.30	50	0.020	0.206
1.0	0.30	50	0.10	0.196
1.0	0.30	50	0.40	0.201

Mixtures were prepared as shown in Table X and the solutions obtained after removing the solid by centrifugation were used for the determination of unadsorbed quinine bisulfate. The analytical procedure was as follows: Aliquot portions of the aqueous solutions were evaporated to dryness, to remove excess of hydrochloric acid. The residues were just neutralized with aqueous sodium hydroxide and again evaporated to dryness. They

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were then extracted with absolute alcohol and the alcoholic extracts evaporated to dryness. These were treated with hydrochloric acid to yield quinine dihydrochloride and after repeated evaporations to remove excess of acid, the alkaloidal salt was titrated[1] with 0.01 *N* NaOH and the corresponding amount of quinine bisulfate calculated from these titrations. The quantities of quinine bisulfate thus found were subtracted from the amounts of this salt originally present, and the differences given in Table X as the g. adsorbed per 1.0 g. of fuller's earth.

These results show that in the case of the ratio of 0.15 g. of quinine salt per 1.0 g. of fuller's earth, which is very near the quantity just completely adsorbed in water alone, the increase of acidity has relatively much less effect in diminishing the adsorption than when the ratio is 0.3 g. salt per 1.0 g. of fuller's earth.

As in the case of the dilution experiment, the retarding effect here is of no serious consequence, provided the amount of fuller's earth used is sufficient for complete adsorption of the amount of alkaloid present.

Effect of Ethyl Alcohol on the Adsorption of Quinine Bisulfate and of Methylene Blue by Fuller's Earth.—In this as in the other experiments, two ratios of fuller's earth to material to be adsorbed were selected, one being that at which almost complete adsorption occurs and the other representing insufficient earth to adsorb all the alkaloid or methylene blue present. The results are shown in Tables XI and XII. It is seen that little effect is produced by the alcohol when the larger proportion of fuller's earth is present, but that the reduction caused by the alcohol in the other case is quite marked. It is, therefore, apparent that, even in presence of very large quantities of alcohol, complete adsorption can be obtained provided fuller's earth is used in the proper proportion.

TABLE XI.—EFFECT OF ETHYL ALCOHOL ON THE ADSORPTION OF QUININE BISULFATE BY FULLER'S EARTH.

(Each mixture rotated one-half hour and the solid removed by centrifugation.)

G. English fuller's earth.	G. quinine bisulfate.	Volume of mixture. Cc.	Vol. % alcohol in mixture.	G. quinine bisulfate adsorbed per 1.0 g. fuller's earth.
1.0	0.15	50	10	0.149
1.0	0.15	50	20	0.148
1.0	0.15	50	40	0.147
1.0	0.15	50	70	0.147
1.0	0.30	50	10	0.265
1.0	0.30	50	20	0.257
1.0	0.30	50	40	0.228
1.0	0.30	50	70	0.221

[1] Method of E. Elvove, "Fixing Power of Alkaloids for Volatile Acids and Its Application to the Estimation of Alkaloids with the Aid of Phenolphthalein or by the Volhard Method," *Hyg. Lab. Bull.*, P. H. S., 54, 1909.

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TABLE XII.—EFFECT OF ETHYL ALCOHOL ON THE ADSORPTION OF METHYLENE BLUE BY FULLER'S EARTH.

(Each mixture rotated one-half hour and the solid removed by centrifugation.)

G. English fuller's earth.	G. methylene blue.	Volume of mixture. Cc.	Vol. % alcohol in mixture.	G. methylene blue adsorbed per 1.0 g. fuller's earth.
0.5	0.075	50	10	0.1497
0.5	0.075	50	20	0.1497
0.5	0.075	50	40	0.1495
0.5	0.075	50	70	0.1486
0.5	0.150	50	10	0.2330
0.5	0.150	50	20	0.2334
0.5	0.150	50	40	0.2270
0.25	0.075	50	70	0.1976

Effect of Cane Sugar on the Adsorption of Quinine Bisulfate by Fuller's Earth.—This experiment was made in the same manner as the preceding. The results are given in Table XIII and show that almost no reduction of the adsorption occurs when either the higher or the lower ratio of fuller's earth is used.

TABLE XIII.—EFFECT OF CANE SUGAR UPON THE ADSORPTION OF QUININE BISULFATE BY FULLER'S EARTH.

(Each mixture rotated one-half hour and the solid removed by centrifugation.)

G. English fuller's earth.	G. quinine bisulfate.	G. cane sugar.	Volume of solution. Cc.	G. quinine bisulfate adsorbed per 1.0 g. fuller's earth.
1.0	0.15	2.5	50	0.145
1.0	0.15	5.0	50	0.143
1.0	0.15	10.0	50	0.144
1.0	0.15	17.5	50	0.144
1.0	0.30	2.5	50	0.257
1.0	0.30	5.0	50	0.257
1.0	0.30	10.0	50	0.256
1.0	0.30	17.5	50	0.254

Summary.

A comparison of the adsorptive capacities of 36 samples of fuller's earths and other clays showed that English earth is superior to any of the domestic fuller's earths except one, the exact source of which could not be learned. Domestic bentonite exhibits a higher adsorptive power than the English samples of fuller's earth, but on account of its exceptional capacity for retaining water, it cannot be used to advantage in cases, such as the present, where a sharp separation of solid and solution is essential.

It was found that the adsorption of quinine bisulfate and methylene blue by fuller's earth increased with time of contact but at a gradually diminishing rate. It was also found that the amounts adsorbed continued to increase with amount of excess present. Maxima were not observed in the case of either the time factor or the concentration factor.

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In the case of both quinine bisulfate and of methylene blue the free base only is adsorbed from the aqueous solution when brought in contact with fuller's earth. The acid component of each compound unites with calcium derived from the fuller's earth and remains in the aqueous solution.

When equal amounts of quinine bisulfate and methylene blue are simultaneously present in an aqueous solution shaken with fuller's earth, both compounds are adsorbed to approximately the same extent. The sum of the two components is about 25% greater than the amount of either adsorbed separately.

When the same portion of fuller's earth is first shaken with methylene blue and then with quinine bisulfate, a small amount of the latter compound is taken up and only a trace of the former liberated. When the procedure is reversed, considerably more methylene blue is adsorbed and a fairly large proportion of the quinine bisulfate is displaced from its combination with the fuller's earth. The results show that under the special conditions of this experiment, fuller's earth exhibits a distinct preference for methylene blue.

Dilution of the aqueous solution, in the case of quinine bisulfate, does not diminish appreciably the amount adsorbed when the ratio of earth to alkaloid is approximately that required for complete adsorption. In the case of a ratio of earth which is insufficient for complete adsorption, dilution causes a distinct reduction in the amount adsorbed.

Increase of acidity of the aqueous solution, likewise, does not diminish the amount of quinine adsorbed in case the ratio of earth is just sufficient for complete adsorption. With less earth than sufficient for complete adsorption a distinct reduction in the amount of adsorbed alkaloid follows an increase in acidity of the aqueous medium.

Ethyl alcohol diminishes the adsorption only in cases where the ratio of earth used is insufficient for complete removal of quinine or of methylene blue.

The presence of quite large amounts of cane sugar was found to exert no retarding influence upon the adsorption of quinine bisulfate by fuller's earth.

In conclusion it appears that the adsorptive power of fuller's earth is exerted particularly towards certain compounds, characterized by distinct basicity and that in the case of salts, only the base unites with the fuller's earth. No marked selectivity was found in the case of the two compounds forming the basis of the present experiments. The amount adsorbed in a given time is a function of ratio of earth to adsorbable material and except with insufficient earth for complete adsorption, is independent of dilution, acidity or presence of non-adsorbable neutral material.

WASHINGTON, D. C.

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NOTE.

The Action of Trioxymethylene on the Various Hydrocarbons in the Presence of Aluminum Chloride.—In a paper published by Kokatnur and myself on the "Action of Trioxymethylene on the Various Hydrocarbons in the Presence of Aluminum Chloride" (THIS JOURNAL, 36, 1529 (1914)) it was stated that so far as we know, trioxymethylene had never been used with aluminum chloride. Professor Nastukof has called attention to the fact that he published a paper in 1913 in the Imperial Russian Society in Baku in which he mentioned the action of trioxymethylene upon naphtha hydrocarbons in the presence of aluminum chloride. As the article referred to is not abstracted and the publications of the Baku Society do not appear in the general chemical libraries of this country, we had no means of obtaining reference to the article. Attention is called to the introduction of the above-mentioned article in which reference is made to experiments by Kritchevsky and myself which began as early as 1911. Extended experiments were made on the aldehydes, an outline of which was given at the meeting of the Eighth International Congress of Applied Chemistry in New York, 1912, in a paper, an abstract of which appeared in the proceedings of the Congress, entitled "the Action of Chloralbromal and Aluminum Chloride on the Phenolethers." Naturally, in testing out the various aldehydes, trioxymethylene was one of the first to be tried. But as chloral gave better crystallized compounds than the other aldehydes, it was taken up first. The above reason for taking up chloral and bromal first was given in presenting the paper at the New York Congress. I also indicated at that time that we were following up these experiments as rapidly as possible. The work is still under way. G. B. FRANKFORTER.

UNIVERSITY OF MINNESOTA,
MINNEAPOLIS, MINN.

CORRECTION.

Mr. R. de M. Taveau has called our attention to the fact that Purdie and Lander in 1898 (*J. Chem. Soc.*, 73, 287 (1898)) found that silver malate and silver lactate give, in part, ethers along with esters on treatment with alkyl iodides. We had overlooked this in the statement made in our paper, THIS JOURNAL, 39, 2711 (1917). In the cases studied by Purdie and Lander the hydroxyl group was in the alpha position. Ciscamphonolic acid, which we used, has the hydroxyl group in the gamma position.

W. A. NOYES,
G. S. SKINNER.

NEW BOOKS.

The Chemists' Year Book, 1917. Edited by F. W. ATACK, assisted by L. Whinyates. Two volumes. London: Sherratt and Hughes, 1917. 1030 pp.

A collection of chemical and physical tables does not offer great oppor-

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tunity for variety of treatment, except in the selection and arrangement of the material. The little work before us presents the standard data upon which chemists and physicists depended. In form and content it more nearly resembles the Chemiker-Kalender than any other book with which we are familiar, but it is a distinct improvement upon it in at least two respects. There is a fifteen-page index and by the use of a more open-faced type legibility is increased without enlarging the size of the page.

If any fault is to be found with the Year Book and other works of this class, it must be on account of the ground they attempt to cover rather than for sins of omission. One cannot well complain about the introduction of brief sections on qualitative analysis, volumetric analysis, etc., but it has always seemed to the reviewer, in twenty years' experience with the Chemiker-Kalender, that much could be omitted without lessening the value of the book. This criticism applies also to the Year Book, which devotes only 387 pages to the discussion of twenty-seven topics of such varied range as Water Analysis, Portland Cement, Oils and Fats, Paints and Pigments, Beer and Spirits, Cellulose and Paper, Physiological Chemistry, India Rubber, Tobacco, Photography, etc. It is quite evident that, in such a limited space, not much more than a smattering of information on any one topic is given. Perhaps, however, it is only fair to assume that the editor knows what is called for. In any case he is to be commended for having put into our hands such a wealth of information in convenient form. C. E. W.

A Systematic Course of Qualitative Chemical Analysis of Inorganic and Organic Substances. By HENRY W. SCHIMPF. Third edition, revised. New York: John Wiley & Sons, Inc., 1917. Pp. ix + 187.

Professor Schimpf's book is written for students in Pharmacy, but this in no wise makes it less valuable for students of Chemistry.

Part I, 16 pages, is a review of chemical terms. Part II, 117 pages, is entitled "Identification and Separation of Inorganic Bases and Acids." It includes, however, a list of 17 organic acids. Part III, 54 pages, is devoted to the "Qualitative Analysis of Organic Substances."

The general style of the book is characterized by an abundance of charts presenting in a concise way the essential procedures, and also by numerous reactions. These reactions are all of the good, old-fashioned type as evidently the author sees no virtue in the theory of ions as an aid in teaching qualitative analysis. From a literary standpoint the book suggests an informal lecture style.

In the reviewer's opinion, the chief value that Professor Schimpf's book has for chemists is its copious treatment of the methods for examining the commoner organic substances. After all, why should they not be included in elementary qualitative analysis? The trend of the times

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seems to show that in the near future the detection of ethyl alcohol will be of more importance than, for example, tests for cadmium or strontium.

C. W. FOULK.

Principles of Agricultural Chemistry. By G. S. FRAPS, PH.D. Chemist, Texas Experiment Station, Agricultural and Mechanical College of Texas. State Chemist. Second edition, pp. 501. The Chemical Publishing Company, Easton, Pa.

The author states that this revision of the first edition, which was published in 1912, was undertaken for the purpose of making such changes and additions as were required to keep it abreast of the times and for the purpose of including recent work on "soil organisms, the nutritive value of proteids, and productive value of feeds."

The book is divided into twenty-four chapters dealing with the essential features of plant nutrition, the relation of the plant and the atmosphere, the origin, classification, physical properties, water relations, and chemical composition of soils. A chapter is devoted to active plant food and water-soluble constituents of the soil, and the chemical changes, deficiencies, and losses and gains of the soil. The discussion of manures and the composition, purchase and sources of fertilizers is covered in three chapters. A reasonable amount of space is devoted to plant constituents and the chemical composition of plants and feeding stuffs. In the remainder of the book the author covers the general subject of digestion, the utilization of food, and the general fundamental questions connected with the rational feeding of farm animals.

The discussion of feeds and feeding, while furnishing much useful information to the ordinary student, is primarily of value to those who are desirous of fitting themselves to engage in research work connected with human and animal nutrition. In fact, these particular phases are discussed perhaps with more thoroughness and completeness than in those works on cattle feeding which are designed primarily for use by students who wish to study the question solely in its relation to animal production.

The chapter on "Origin of Soils" is usually covered in courses in geology. The author, however, evidently intended this work to cover all of the subjects discussed, even though they may have been covered by the student in part in other courses. It is a matter of convenience to a student to have all of these various subjects covered in one book, although it is more or less of an innovation as compared with previous books on agricultural chemistry and its various subdivisions which have been published in this country.

In discussing the assimilation of nitrogen by the legumes in the chapter on "Chemical Changes," the author makes no mention of the work with peas by Atwater which was published in 1884 showing unquestionably that they had assimilated atmospheric nitrogen.

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In the chapter entitled "Soil Deficiencies" it is unfortunate that the author in discussing experiments with burned lime or ground limestone, particularly at the Pennsylvania Agricultural Experiment Station, did not give more fully the conditions under which the experiments were conducted. The fact is that the author and other writers have accepted certain statements regarding these tests without analyzing the conditions, whereas Dr. Frear of that Station, in published articles, has stated essentially that, in view of the manner in which the experiments were conducted and the amounts of lime used, quite erroneous conclusions have been drawn by others from the experiments. A careful study of the experiments at the Maryland Station would reveal certain discrepancies indicating an apparent wide variation in the character of the soil or other features which do not justify a sweeping denunciation of burned lime as compared with ground limestone. The general effect of the quotation of these two experiments is to place slaked or burned lime in a somewhat false position as concerns its efficiency and value for agricultural purposes as compared with ground limestone. The latter has unquestioned advantages, but not to the extent which the reader would be led to believe.

In the same chapter regarding toxic substances in soil, the writer states that it is possible that some soils may contain injurious substances besides alkali or acids. This makes one wish that he had been more specific in view of the work of Conner of Indiana and Ruprecht of Massachusetts on the toxicity of aluminum compounds and the well-known toxicity of certain iron and other salts.

Referring to the manufacture of acid phosphate in the chapter on "Sources and Composition of Fertilizers," the author calls attention to the rotting of bags and the stickiness which results when an excess of acid is used. The fact is, however, that careful manufacturers avoid this or by the addition of very small amounts of calcium carbonate neutralize the excess of free acid, whereby the difficulties mentioned are overcome. Unfortunately the reader might infer that the rotting of bags and the presence of free sulfuric acid and phosphoric acid were matters of common occurrence, whereas the reverse is true.

In the chapter entitled "Purchase and Use of Fertilizers" it is stated by the author that there is no justification for the claim that sulfate of lime may liberate soil potash, yet European experiments are on record showing far greater percentages of potash in plants grown on soil to which sulfate of lime had been applied than on corresponding soil where none had been used. It is difficult to harmonize these particular experiments with this statement. And further on it is made to appear as if it were immaterial in the fertilization of corn whether acid phosphate at the rate named or raw rock phosphate was used as the source of phosphoric

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acid. While this may be true possibly in the case of some special soils highly charged with acid organic matter, experiments at the Tennessee, Indiana, Massachusetts and other experiment stations do not seem to justify conveying such an impression.

On the whole, the book is a most valuable one which should be in every agricultural college and experiment station library and in the hands of every advanced agricultural student. In view of the volume of work represented, it is relatively free from typographical and other errors. Time might be taken to enumerate several of these errors, but the book is of so much importance and value that it would be supercritical to do so and indicative of a lack of proper appreciation of the vast amount of work and detailed care which is evidenced throughout. Agricultural chemists in this country and abroad will recognize this book as a most valuable acquisition.

H. J. WHEELER.

Handbook of Antiseptics. By HENRY DRYSDALE DAKIN, D.Sc., F.I.C., F.R.S., AND EDWARD KELLOGG DUNHAM, M.D., Emeritus Professor of Pathology, University and Bellevue Hospital Medical College, Major, Medical Officers Reserve Corps, U. S. Army. IX, 126 pp., tables and figures. New York: The Macmillan Company. October, 1917. Price, $1.25.

In their new book on antiseptics, Dakin and Dunham have given a more practical and valuable account of antiseptics than is generally found in most bacteriological texts. In a series of eight chapters covering 126 pages the authors have discussed the general considerations of antisepsis, the various types of antiseptics, their preparation, the factors which affect their germicidal value and the type of antiseptic most desirable under certain conditions. One is impressed with the fact that the emphasis placed upon the different phases in the rather complex problem of proper disinfection is well balanced. The criticism of the antiseptics, which in the past have found rather general use, is very much to the point while the statements regarding the use and composition of the newer antiseptics is clear, concise and satisfactory. One of the most interesting sections of the book is that dealing with the antiseptics of the chlorine group, namely, "Hypochlorous acid and its sodium or other salts, Chloramine-T and Dichloramine-T." A detailed account of the technique in some procedures has been omitted as being beyond the scope of the book, but in such instances references to the original publications are given so that the reader may, without any great inconvenience, obtain most of the available information concerning such procedures. The authors have shown a singularly fortunate appreciation of the obstacles and difficulties which are encountered in the preparation, testing and use of various antiseptics. Dakin and Dunham have collected in a small and convenient volume material which has been scattered throughout various publications, and especially data on the antiseptics which have been found most

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useful in the treatment of wounds during the war. The book, which does not pretend to be an exhaustive treatise on antiseptis, is clear, concise and adequate and should be most helpful to both the physician in the field and the investigator interested in the problem of antiseptics.

JOEL A. SPERRY, 2ND.

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THE JOURNAL

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American Chemical Journal

(Founded by Ira Remsen)

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF CLARK UNIVERSITY, I, 3.]

AN INVESTIGATION OF THE REACTION BETWEEN ANTIMONY AND SOLUTIONS OF SODIUM IN LIQUID AMMONIA.[1]

BY EDWARD B. PECK.

Received September 25, 1917.

I. Introduction.

Joannis[2] has shown that solutions of the alkali metals in liquid ammonia react with certain heavy metals which are themselves insoluble in this solvent. He found that compounds are formed with antimony, lead, bismuth and mercury, their composition corresponding to the formulas Na_3Sb, NaPb, $NaPb_4$, KPb_2, NaBi, $NaHg_{18}$, etc.

Kraus,[3] in a series of unpublished investigations, found that the compounds described by Joannis react further with an excess of the heavy metal to form compounds richer in the heavy metal. He also found that tin, tellurium, selenium and sulfur behave similarly. These compounds were found to possess electrolytic properties in dilute solution. For lead, Kraus[4] found that two-gram atoms of metal were deposited at the anode for every equivalent of electricity passing through the solution.

[1] A thesis presented to the Faculty of Clark University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Joannis, *Compt. rend.*, 113, 797 (1891); 114, 595 (1892).

[3] Kraus, unpublished observations.

[4] Kraus, THIS JOURNAL, 29, 1557 (1907).

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At the suggestion of Dr. Kraus, Posnjak[1] and later Smyth,[2] studied these sodium-lead compounds and found that the equivalence of lead and sodium in solution does not correspond to an integral number. Smyth[3] found, on electrolyzing these solutions, that 2.26 gram atoms of lead are deposited on the anode for one equivalent of electricity. This value was found to be independent of the concentration and the current density. Smyth also attempted the analysis of these solutions, but his results were not conclusive owing to the reaction of sodium with the ammonia to form the amide according to the equation

$$Na + NH_3 = NaNH_2 + {}^1/_2H_2.$$

This reaction was facilitated by the slowness of the action of the sodium on the lead.

The present investigation was undertaken for the purpose of securing further data on the compounds formed in the interaction between the alkali metals and the heavy metals. Antimony was chosen in place of lead for the reason that it reacts rapidly enough to prevent the formation of an appreciable amount of amide.

Other compounds of sodium and antimony have been obtained as alloys. Gay-Lussac and Thenard[4] first observed that antimony and sodium react with the evolution of heat and light. Mathewson[5] has studied the alloys of antimony and sodium by the method of thermal analysis and found the compounds Na_3Sb and NaSb.

Joannis[6] allowed solutions of sodium in liquid ammonia to react with antimony until the color of the sodium solution disappeared. This gave a dark brown precipitate and a pale yellow solution. His analysis showed the compound to be Na_3Sb. This compound was very readily oxidized in air or water. Kraus[7] found that this compound reacts further with antimony to give a very soluble compound having a deep red color in concentrated solution. The present investigation was undertaken at the suggestion of Dr. Kraus with the hope that this method would throw further light on the physical chemical properties of pure metallic compounds.

II. Apparatus.

The method of carrying out this work was to introduce a weighed amount of sodium with liquid ammonia and an excess of antimony of known weight into a two-compartment bomb which was then sealed off

[1] Posnjak, See Smyth, THIS JOURNAL, 39, 1299 (1917).

[2] Smyth, Ph.D. Dissertation, M. I. T. (1915); THIS JOURNAL, 39, 1299 (1917).

[3] Smyth, *Loc. cit.*

[4] Gay-Lussac and Thénard, "Recherches Physico-Chemique," Paris (1811).

[5] Mathewson, *Z. anorg. Chem.*, 50, 192 (1906).

[6] Joannis, *Loc. cit.*

[7] Kraus, *Ibid.*

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and the reaction allowed to run to completion. The phases were separated for analysis by decanting the solution into the second compartment, leaving the excess antimony behind to be washed by distilling ammonia over from the solution. The ammonia was then distilled out of the bomb and absorbed in weighed water bottles and the weight of antimony which had reacted was obtained by difference.

The apparatus used for filling the reaction bomb is shown diagrammatically in Fig. 1.

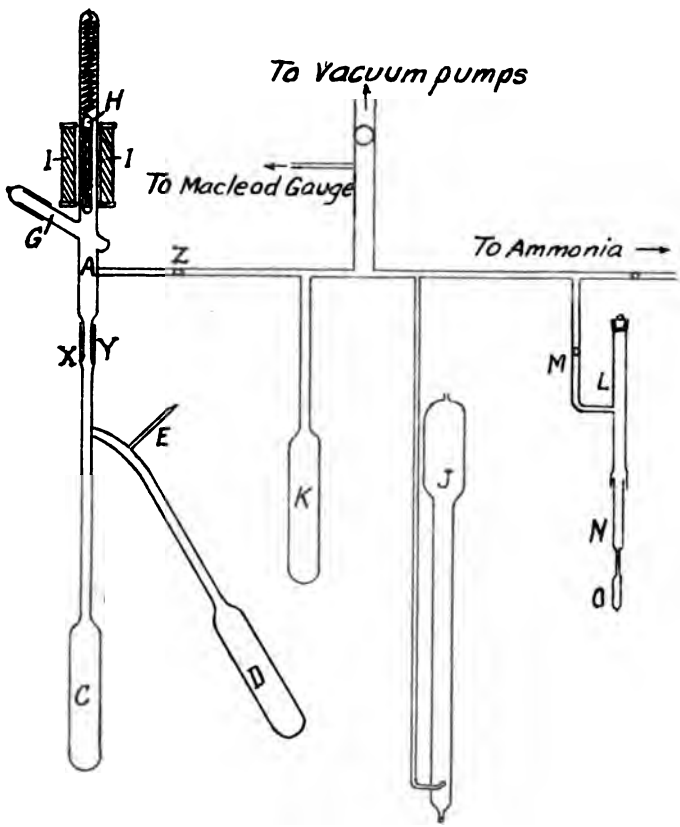

Fig. 1.

The filling device A was connected to the vacuum pumps and the ammonia cylinder by the horizontal glass tube provided with a stopcock Z. The bomb C was connected to the bottom of the filling device by a glass sleeve sealed with de Khotinsky cement. The lower part of the filling tube Y was made of the same diameter as the arms of the bomb and the end of the vertical arm of the bomb was provided with a sleeve, X, just wide enough to slip over the lower end of the filling tube.

The bombs consisted of two cells, C and D, of from 30 to 50 cc. capacity,

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connected by arms of about 6 mm. internal diameter and 20 cm. long. On the bent arm was connected a narrow tube, E, through which the ammonia was distilled off after the reaction and washing was completed. The tube from the branch to the enlarged sleeve was about 10 cm. long to allow sufficient room for sealing off the bomb after filling. A weighed amount of antimony was placed in the bottom of the reaction chamber C of the bomb before it was connected to the filling device. The sodium which was introduced in a manner similar to that used by Smyth[1] was sealed up in a small glass capsule, and this capsule placed across the filling tube through the side tube G. A notch opposite the side tube held the sodium capsule in place where it could be dropped into the bomb by breaking it in two. The side arm had a cap which was sealed on with de Khotinsky cement. The earlier bombs were made of ordinary soda glass, but this was later changed to a very strong glass of low temperature coefficient as earlier bombs had exploded.

When the apparatus had been evacuated and the desired amount of ammonia distilled into the bomb, the sodium capsule was broken and allowed to drop into the bomb. The capsule was broken by the electromagnetic hammer H which consisted of a piece of soft iron sealed up in a glass tube and suspended by a steel spring from the top of the filling tube. This hammer was actuated by means of the solenoid I placed outside the tube.

The manometer tube J showed the pressure on the solution and also acted as a safety valve to adjust the pressure at which the ammonia was run into the apparatus. This was so designed as to allow the excess ammonia to escape under any desired head of mercury. The chamber K was an ammonia reservoir to be used for drawing off ammonia from the bomb or as a reservoir of ammonia gas in filling the sodium capsule.

The weighed charges of sodium were put up by means of the device on the right of the figure. The straight tube L was connected to the vacuum system and ammonia supply by a side tube, M, provided with a stopcock. The top of the tube L was provided with a carefully ground stopper and at the bottom with a flange to allow a tube of the same diameter to be sealed on after the manner described above in connection with the bomb and filling tube. The tube N, about 8 cm. long and 0.4 cm. internal diameter, was drawn down to a fine capillary, on the end of which was the capsule O for receiving the sodium. This capsule was about 4 cm. long and 0.2 cm. internal diameter and file scratched across the middle to facilitate breaking with the hammer H. When a larger capsule was required a bulb was blown on the end. The lower end of the capsule was left open through a capillary opening so that the whole tube NO could be thoroughly cleaned and dried. Then the lower end of the cap-

[1] Smyth, *Loc. cit.*

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sule was sealed and the whole tube weighed and attached to D. A piece of freshly cut sodium was dropped through the top of L into N and a small glass weight placed on it. The apparatus was then evacuated. When all the air had been removed, the sodium was softened by heating with an oil bath. As soon as the sodium began to collapse, a slight pressure of ammonia from K was applied through M, which drove the sodium through the capillary to the bottom of the capsule, leaving the oxide behind. It was necessary to avoid overheating the sodium, as otherwise it attacks the glass. It was also necessary to have the capillary clear and the sodium quite free from the center of the capsule where it was later to be broken open.

With the capsule filled with pure sodium, it was sealed off at the capillary. The tube N was opened at the capillary by blowing a hole through the tip. It was then removed from the upper tube and cleaned, after which it was weighed together with the filled capsule. This, together with the original weight, gave the weight of sodium in the capsule by difference. This weight of sodium was checked by weighing the filled sodium capsule and weighing again after the sodium had been removed.

The antimony used was Kahlbaum's, and came in bars. This was sawed into pieces weighing about 0.6 g. and polished so that there were no loose pieces or fine dust. If fine antimony was used, it was found that very small pieces were carried with the solutions in decanting, thus giving inaccurate results in the analysis.

The ammonia was put up in a steel cylinder over sodium in the manner described by Kraus.[1] The hydrogen was blown off and a pure ammonia obtained by this method.

III. Manipulation.

The apparatus will probably be better understood by describing a typical run. The sodium capsule was placed across the filling tube and the side arm closed with its cap. Then a weighed piece of antimony was placed in the vertical chamber of the bomb and the bomb sealed to the filling tube. This made a closed system which was evacuated by means of a pair of rotary oil pumps. The pressure was reduced to about 0.0001 mm. of mercury and the system carefully tested with a MacLeod gage for leaks. In exhausting, the bomb was heated to drive the gas out of the antimony.

When the apparatus was found to be tight, ammonia was condensed in the vertical chamber of the bomb by surrounding it with a bath of liquid ammonia and then opening the valve to the cylinder containing the pure ammonia. When a sufficient quantity of ammonia had been condensed, the sodium was introduced by breaking the capsule in two with the electro-magnetic hammer. The intensity of the hammer blow

[1] Kraus, This Journal, 30, 1205 (1908).

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could be adjusted by raising or lowering the solenoid outside the tube. Generally, a very light blow sufficed, and the capsule broke clean without shattering. This later was important in getting the check on the weight of sodium.

The first stage of the reaction, which was very rapid, was allowed to go on at the temperature of the ammonia bath. The reaction could be hastened by stirring which was accomplished by removing the bath from the bomb chamber and placing it around the auxiliary chamber K. After a small amount of the ammonia had been boiled off, the bath was returned around the bomb. As soon as the blue color of the sodium solution had disappeared, the bomb was sealed off at F.

The bomb was then hung up with the solution chamber of the bomb in a bath of running water. This was found necessary in order to prevent the ammonia from distilling off from the solution into the second chamber, thus changing the concentration of the solution. The bomb was left undisturbed for from two months to a year in order that the reaction might proceed to completion, after which the contents were separated and analyzed.

The separation was carried out as follows: The solution was poured from the chamber C into the chamber D, leaving the excess antimony and the empty sodium capsule behind. These were washed several times by distilling the pure solvent from the solution back to the original chamber. The distillation was accomplished by immersing the chamber C in ice-water and leaving the solution at room temperature. The washing process was continued until the condensed ammonia was colorless.

When the washing was complete, the various components were separable for analysis. The chamber with the solution was immersed in a bath of boiling ammonia to reduce the pressure in the bomb. Then the narrow side tube E was broken off near the end, the bomb removed from the bath, and connected to a train of two weighed water bottles. These bottles contained gas-free water and absorbed the ammonia, the weight of which was obtained by difference. The bomb had to be removed from the bath before connecting to the water train or the water would suck back into the bomb and spoil the analysis. Care had to be taken to boil the solution from the top by heating with the hand or the solution would superheat and boil over. When the ammonia was all driven off, the bomb was broken open, the excess antimony and the excess sodium capsule were weighed, which gave all the data necessary for an analysis.

IV. Behavior of the Compound.

Before turning to the analytical results it will be of interest to discuss the behavior of the solutions and the properties of the compounds. When sodium dissolves in liquid ammonia, it forms a deep blue solution. As the solution reacts with antimony, which is itself insoluble, the color dimin-

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ishes and a dark brown precipitate collects in the bottom of the cell. Finally, the solution becomes light yellow in color. This part of the reaction is very rapid, being completed in an hour or two, and is attended by the evolution of considerable heat. The compound formed at this stage is evidently the one studied by Joannis,[1] Na_3Sb. The next change observed is the appearance of a deep red-colored solution, and the general disappearance of the precipitate. The color deepens until all of the precipitate has disappeared. This last reaction is much slower than the first, because of the slight solubility of the reacting compound. If these solutions could be thoroughly stirred the final equilibrium would be attained much more rapidly. In this work the bombs were only occasionally shaken. Care should be exercised in handling the bombs, as they are liable to explode.

A test for the side reaction of sodium with ammonia to form the amide was carried out as soon as the first compound was completely formed. This was done by attaching a eudiometer tube to the apparatus. The lead tube from the apparatus was connected to the supply tube A and blew off under a layer of mercury into the eudiometer tube, filled with gas-free water. Ammonia was rapidly boiled off from the solution for about ten minutes, and in that time about 0.3 cc. of insoluble gas appeared over the water. This shows that there was no appreciable amount of amide formed.

The residue from these solutions was dark brown in color when covered with a thin film of ammonia, but when all the ammonia was driven off there remained a bluish gray metallic residue. This residue could be readily crumbled and had no crystalline structure, the latter probably due to the conditions of precipitation. This product oxidized only slowly in air and in water.

The compound redissolved in ammonia, but with some difficulty if all the ammonia had been driven off. From some of the solutions, which apparently were not saturated, a metallic mirror was deposited on the walls of the bomb. This layer was redissolved only with the greatest difficulty. The nature of this deposit has not been determined.

V. Experimental Results.

The results of the analyses are shown in Table I.

The concentrations of the solutions are expressed in gram atoms per liter of ammonia. The volume was calculated by using the value of Keyes and Brownlee[2] for the specific volume of ammonia at 20° (1.6387), and assuming the volume of the solution to be the same as that of the pure ammonia. The latter assumption, of course, is an approximation.

[1] Joannis, *Loc. cit.*

[2] Keyes and Brownlee, "Thermodynamic Properties of Ammonia," p. 14. John Wiley and Sons, Inc., 1916.

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TABLE I.

Series A.			Series B.				
Wt. of Na.	Wt. of Sb.	Sb/Na.	Wt. of Na.	Wt. of Sb.	Sb/Na.	G. NH_3.	G. atoms Na. Liter NH_3.
0.2021	2.445	2.315	0.00237	0.0152	1.198	12.926	0.0049
0.1986	2.3345	2.249	0.00610	0.0594	1.853	4.352	0.0372
0.1328	1.5310	2.206	0.00993	0.0837	1.613	6.713	0.0393
0.0745	0.9067	2.329	0.01100	0.1147	1.978	7.852	0.0375
0.0592	0.6681	2.1595	0.02580	0.2924	2.169	6.974	0.0982
0.0288	0.3379	2.246	0.02880	0.3379	2.246	6.291	0.1229
0.0284	0.2441	1.650	0.03071	0.3583	2.333	1.874	0.4347
..	..	..	0.09115	1.0799	2.267	..	..
..	..	..	0.4080	4.8049	2.254	8.673	1.2482

In Series A the amount of ammonia was not determined as it was expected that the values would be independent of the concentration, as was found to be the case with lead. The results showed, however, that there was a concentration effect. In Series B, the concentration was determined. The results are treated graphically in Curves A and B, Fig. 2.

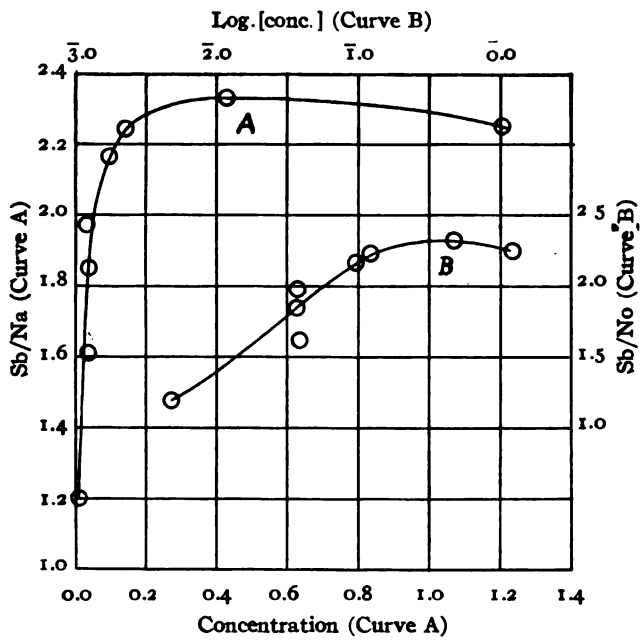

Fig. 2.

In Curve A, the ratio Sb/Na is plotted against the concentration of sodium and in Curve B the ratio Sb/Na is plotted against the logarithm of the concentration for the purpose of redistributing the points for dilute solutions. In plotting Curve A, the curve in the concentrated region is in a measure governed by the results of Series A. These values justify

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drawing the curve through the points of higher concentration, for there are several values that certainly would be on that curve if their exact concentration had been determined.

The ratio Sb/Na increases very rapidly with concentration in dilute solution to a maximum of 2.3 at a concentration of about 0.4 N. There is a slight decrease in the ratio Sb/Na beyond this concentration which might become constant if the concentrations were corrected for change in density. Mr. Allison,[1] working in this laboratory, has obtained similar results for tellurium and sodium. He obtained a maximum for the ratio Te/Na = 1.98 at a concentration of about 0.1 N with respect to sodium. The fall in the curve beyond the maximum in concentrated solutions is more pronounced than for antimony and sodium. It is apparent from these data that, if this investigation had been confined to a range of concentration above 0.4 N, it would have appeared that the ratio Sb/Na were substantially independent of concentration, as Smyth[2] found for lead. It appears from this work that a concentration effect might have been found in the lead-sodium equilibria had they been studied at higher dilutions.

The precision of this work was limited entirely by the manipulation of the solutions in the bombs. The smallest weight involved, namely, that of the sodium, was about ten times smaller than that of the antimony. This weight could be determined very accurately, in most cases to 0.02 mg., as was shown by the checks. These solutions may not have reached equilibrium and this apparently is the chief source of error in this work. Indeed, the slight decrease from the maximum may be due to this phenomena, for these solutions were very viscous and some showed a precipitate which would suggest this explanation. One result, at a sodium concentration of 0.0219 N, gave a value Sb/Na = 3.142. This result agrees with no other analytical results, but a single similar result was obtained in the electrolysis of very dilute solutions at the temperature of liquid ammonia.

VI. Electrolysis of the Solutions.

The electrolysis of these solutions was undertaken for the purpose of determining the electrolytic properties of the metallic compounds in solution. This part of the work was carried out in a manner similar to that of Smyth.[2] The apparatus used for the electrolysis is shown diagrammatically in Fig. 3.

The cell A had a capacity of 150 cc. and was calibrated at 10 cc. intervals. This cell had two long arms, B and C, through which the electrodes were introduced. The arm B had a side tube, P, through which the sodium capsule was introduced. Instead of an electro-magnetic

[1] Allison, Master's Thesis, Clark University, June, 1916.

[2] Smyth, *Loc. cit.*

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hammer, the capsule was broken open by a glass rod, D, which was fitted into the top of the side tube by a piece of heavy rubber tubing. A blow from outside was transmitted to the capsule by this glass rod. Connection with the ammonia cylinder was made by the tube E at the bottom of the cell and through the tube F to each of the arms of the cell. The cell was set in a Dewar flask, Z, which contained liquid ammonia at its boiling point. The electrodes were suspended from their leads, G and H, which consisted of tubes filled with mercury and supplied with platinum hooks. These tubes slid in glass caps that fitted to the limbs of the cell which were contracted to make well-fitting sleeves for the lead tubes. These fittings were made tight with rubber tubing. These caps through which the leads slid were necessary, as the electrodes had to be both raised and lowered in the cell and removed from the cell for weighing. Tight connections, such as were used in the analytical work, were not necessary, as the cell was opened to the air when the electrodes were removed. A long bar of antimony, which could be lowered to any depth in the solution, served as cathode, while a piece of platinum foil with a surface of 8 cm². was used as anode.

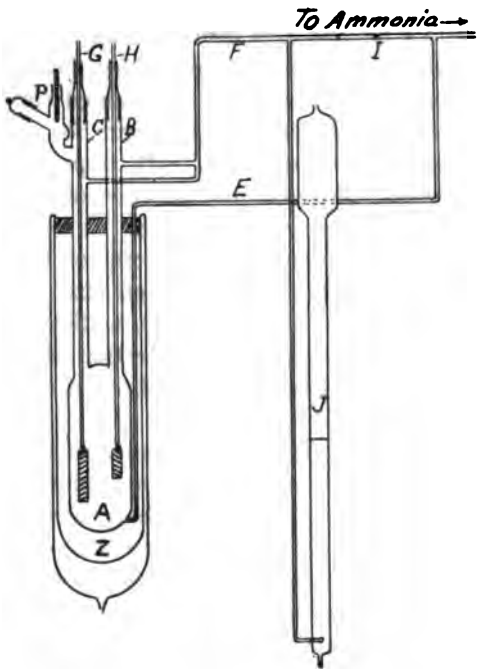

Fig. 3.

Fine pieces of antimony were placed in the cell and the solution made up by introducing the sodium and ammonia after the air had been swept out. This cell was not connected to a high vacuum pump, but alternately filled with ammonia gas and pumped out with a water-jet pump. Finally, the system was swept out by closing stopcock I and allowing the ammonia gas to circulate through from the bottom of the cell and out through the manometer tube J. This same devise was used for stirring the solution. The height of the mercury column was adjustable so that there was no condensation of ammonia in the cell.

As soon as the solution had come to equilibrium, which was within two days, owing to the large surface of metal and the efficient stirring, a series of electrolyses were carried out. A 110-volt storage battery current

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was shunted across a lamp bank to give a current of from two to four milliamperes. The electricity passed was measured by two copper voltameters in series, except for the first electrolysis, when a silver voltameter was used. In the earlier runs the electrodes were weighed and immediately immersed in the solution and the electrolysis begun. The air contained in the antimony was a source of trouble which was partly overcome by placing the electrodes in the limbs of the cell and circulating ammonia gas through the system to remove the air. This was done for a half hour before lowering the electrodes into the cell for the electrolysis.

The deposit on the anode was in the form of crystalline scales of antimony which did not adhere firmly enough to allow stirring of the solution or rotating the electrode.

The electrolyses were run from five to twelve hours. Then the electrodes were raised into the limbs of the cell and there washed by condensing ammonia on them. This was done by opening the stopcock I and allowing the ammonia to enter through the connections at the limbs. The anode was very readily washed, but it was impossible to completely wash the cathode. The cathode was always covered with a heavy black deposit. Various methods of washing were tried. The most successful was to immerse the electrode in water and then dry.

It was found that if the electrodes were short-circuited after electrolysis there was a back current. If this current was allowed to spend

TABLE II.

Voltameter. G. Cu.	Cathode loss.	Anode gain.	Gram atoms of Sb per Faraday. Cathode.	Anode.	Vol. Cc.	Time. Hours.	Current. Mil. amps.
			Series A.				
0.0230[1]	0.0313	0.0336	1.22	1.46[2]	...	..	...
0.0169	0.0841	0.1014	1.315	1.605	...	10.0	2.0
0.0208	0.0360	0.1136	...	1.444[2]	...	5.0	4.0
0.0207	0.0807	0.1862	...	2.375	...	12.0	2–1.5
0.0074	0.0334	0.0678	...	2.419	100	5.0	2.0
0.0264	0.0720	0.3002	...	3.008	120	12.0	4–1
			Series B.				
			0.2652 g. Na used.				
0.01752	0.0122	0.1220	...	1.842	60	..	4.8
0.01280	0.0492[3]	0.0145	1.016	...	120	13.0	2.7
0.05504	....	0.2618	...	1.258	...	11.5	5.5
0.01534	0.0737[3]	....	1.270	...	100	12.5	5.0
0.06662	0.1623	0.3415[2]	...	1.294[2]	95	12.0	6.0—
0.04657	0.2533[3]	0.2732	1.438	1.551	125	11.5	4.0—
0.02984	0.1018[3]	0.1696	0.902	1.503	110	11.0	3.0—
0.02730	0.1041[3]	0.1376	1.009	1.333	100	11.0	2.5
0.02223	....	0.1476	...	1.756	110	7.0	4.0—

[1] Silver voltameter used.

[2] Some deposit lost.

[3] Cathode in good condition.

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itself, most of the black deposit on the cathode was removed. The results of the electrolyses are shown in Table II. In Series A are given the results of two preliminary runs in which the amount of sodium used was not known. The first run was the only one obtained from the first solution. A silver voltameter was used for this run, but the copper voltameters were used in all other runs.

It was noticed that the first runs on these solutions gave the least black deposit on the cathode. This was not found to be true for the first electrolysis on the first solution, Series B, probably because equilibrium had not been attained. The procedure for handling the electrodes had not been developed in Series A, so there was the widest variations in the values for the two electrodes.

There was an abnormal behavior in this series in that the antimony deposit on the anode increased with increase in dilution of the solution to the extraordinary value of 3.0008. A similar value was obtained in the analysis of one of the bombs. The concentration at which these two results were obtained were widely different. The solution in which the electrolysis value was obtained was so dilute that the color intensity was reduced to a point where the solution was transparent even in the large cell. This must have been a concentration a hundred-fold less than for the solution analyzing to Sb/Na = 3.14.

In Series B, which was much more skilfully handled, there was still no close agreement between the two electrodes. Those cathode values indicated with the reference 3 were in good condition, such that an agreement of at least 10% might be expected. This was found in only a few cases, which shows that the process of electrolysis was affected by sources of error which could not be accounted for by the black deposit on the cathode. The possible causes of these irregular values for both electrolysis and the one analysis are so numerous that no definite factor will be discussed until further work has been done.

In spite of the lack of accuracy of these electrolyses, Series B appeared to bear out the results of the analysis that the anions decrease in antimony content with increasing dilution. The results to the contrary and the abnormally high value for the one analysis are no doubt not representative of equilibrium conditions.

VII. Summary.

The results of this investigation show that antimony and solutions of sodium in liquid ammonia react to form a series of compounds. These metallic compounds are electrolytic in nature and their equilibrium is a function of the concentration. In dilute solution, there is a great change of the ratio Sb/Na with the concentration, which at higher concentrations becomes nearly constant, decreasing slightly beyond 0.4 N with respect to sodium. This decrease may be due to lack of equilibrium in

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the viscous concentrated solutions, or it may be due to the fact that the density of the solutions was neglected in calculating the values of the concentrations. The equilibrium must involve not less than two compounds, one of which has a ratio of antimony to sodium greater than two, and one less than two. In dilute solution the compound of low antimony content is present in relatively larger quantities. While the electrolyses have not yielded any conclusive quantitative results, they do show that antimony is present in solution as anion and that more than one atom of antimony is associated with each negative charge. The only compounds previously investigated which bear any resemblance to those just described, aside from the corresponding lead compounds, are the polyiodides.

In conclusion, I wish to express my appreciation of interest and assistance of Professor Charles A. Kraus, under whose direction this work was carried out.

WORCESTER, MASS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF CLARK UNIVERSITY I, 2.]

THE ELECTRICAL CONDUCTANCE OF SOLUTIONS IN BROMINE.

BY EDWARD H. DARBY.

Received October 11, 1917.

Introduction.—The dielectric constant of a solvent is largely determinative of its power to ionize substances dissolved in it, the ionizing power increasing with the dielectric constant according to the Thomsen-Nernst hypothesis. This influence is very marked at low concentrations, but at higher concentrations solvents of low dielectric constant appear to possess an ionizing power comparable with that of solvents of high dielectric constant.

Solutions of strong electrolytes do not obey the mass-action law at higher concentrations and consequently a direct comparison between ionizing power and dielectric constant for different solvents is impossible. According to Kraus and Bray,[1] however, the ionization of a binary electrolyte in any solvent may be expressed as a function of its concentration by the equation

$$\frac{(c\gamma)^2}{c(1-\gamma)} = D(c\gamma)^m + K.$$

Where D, m and K are constants, γ is the degree of ionization and c the concentration. It is thus possible to relate the effect of the dielectric constant on the ionization of a given electrolyte in different solvents by means of the values of the constants D, m and K. Since the relation between ionization and dielectric constant is a very involved one, it is obvious

[1] Kraus and Bray, THIS JOURNAL, 35, 1315 (1913).

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that the ratio of the ionization values for a given salt in two different solvents will depend on the concentration.

Kraus and Bray have shown that the value of K becomes very small for solvents of low dielectric constant. For a dielectric constant below ten, the mass-action constant is too small to admit of ready experimental determination. The value of m increases with increasing dielectric constant, reaching a value a little less than two in the case of solvents of very low dielectric constant. The value of D, however, is practically independent of the value of the dielectric constant of the solvent and lies in the neighborhood of 0.35.[1] It follows then, that a concentration of about 4 N solutions of strong electrolytes in different solvents are ionized to the same extent. At higher concentrations, solutions in solvents of lower dielectric constant should possess the higher ionization.[2]

If a concentrated solution of a strong electrolyte can be obtained in any solvent, it will be highly ionized, irrespective of the value of the dielectric constant of the solvent. Conductance values obtained for solutions in such solvents as amylamine, hydrobromic acid, liquid iodine, etc., beart his out. The strongly electronegative character of liquid iodine makes this solvent a particularly interesting one with which to work, but its dielectric constant has not been measured and a comparison with other solvents is impossible.

The dielectric constant of bromine, however, is 3.18 at 20° and it seemed that, in view of the solvent and ionizing powers of iodine, bromine might exhibit similar properties. Plotnikow and Rokotjan[3] have shown that a number of substances such as IBr, and PBr_5, yield conducting solutions in bromine, although the conductance of such solutions is very low. Judging by the results obtained with other solvents, strong solutions of typical electrolytes in bromine should be very much better conductors than the solutions investigated by Plotnikow.

At the suggestion of Dr. Kraus, an investigation of bromine solutions was, therefore, undertaken. Potassium bromide did not appear to be appreciably soluble in bromine. It was to be expected, however, that salts of the organic nitrogen bases would prove to be soluble and such was found to be the case. Tetramethylammonium bromide was found to be soluble to the extent of about 0.10 N, but this concentration was not sufficiently high for the purpose of this investigation. Trimethylammonium chloride was then tried and found to be extremely soluble. Other salts of organic bases are doubtless soluble in bromine but the investigation has not been extended any further in this direction.

[1] The only marked exception is water, in which case D has the value approximately 2.5.

[2] This result can not well be verified owing to other factors which enter at high concentration, such as viscosity for example.

[3] Plotnikow and Rokotjan, *Ztschr. f. phys. Chem.*, **84**, 365 (1913).

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Trimethylammonium chloride is very readily soluble in bromine, in fact, the salt absorbs bromine vapor so rapidly that it was found necessary to make the salt up into pellets in order to introduce it into the cell. The vapor pressure of the bromine is greatly lowered by the addition of the salt, as is evident from the decrease in color intensity of the bromine vapor over the solution. The color of the liquid also becomes less intense. At high concentrations the solution is transparent with a yellowish color. The viscosity of these solutions increases enormously with concentration. It is evident from these facts that the addition of an electrolyte to bromine has an enormous effect on the condition of the solvent. Wherein this consists, cannot be determined without further investigation.

Apparatus.—The Kohlrausch method was used in determining the conductance of the solutions. A drum-wound bridge of three meters' length was employed, using a telephone and induction coil. Two resistance boxes were employed, one of 111,000 ohms' capacity with Curtis wound coils for higher resistances and an ordinary box for the lower resistances. A variable air condenser was placed in the circuit for the purpose of compensating the effects of capacity and induction.

The temperature was maintained at 18° ± 0.01°, the thermostat being adjusted by means of a thermometer, divided in tenth degrees, and calibrated by the Reichsanstalt.

The cell employed consisted of a glass cylinder about 35 cm. long and 3 cm. in diameter. At the top it was provided with a neck bent at an angle of 90° to the axis of the cylinder to allow of tipping the cell and mixing the solution without danger of loss around the ground-glass stopper. Platinum electrodes, of one cm. square, were sealed into the bottom of the cell by stiff platinum wires to which tubular extensions were sealed extending outside the cell and bent upwards. These tubes were filled with mercury and provided contact with the bridge wires.

The platinum electrodes were not coated with platinum black since polarization effects in bromine are negligible. This necessitated a modification in the method of calibration as usually followed. The constant of a second cell platinized in the usual manner was determined with a potassium chloride solution using salt that had been subjected to repeated recrystallization from conductivity water. A solution of potassium iodide was then made up of arbitrary concentration and saturated with iodine. Using this solution, the resistance of the reference cell and that of the cell used in the experiments were measured. After correcting for the resistance of the leads, the cell constant of the latter cell is obtained at once.

In Table I are given the results obtained in the standardization of the reference cell. The concentration of the solution is given in the first column, the resistance of the solution after correction R is given in the

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second column, the specific conductance L as determined by Kohlrausch is given in the third, and the cell constant $K = LR$ is given in the last column.

TABLE I.

Conc.	R.	L (Kohlrausch).	K.
0.01 N	2800.2	0.001225	3.43029
0.02 N	1429.9	0.002397	3.42749

The resistance of the reference cell with the potassium iodide solution was 2986 ohms, while that for the other was 161.07 ohms. This gives 0.1850 for the constant of the cell employed in this investigation.

Materials.—The bromine used was purified by distillation. The conductance of bromine was so small that it could not be determined with the apparatus available. It was certainly so low as to be entirely negligible.

The trimethylammonium chloride was Kahlbaum's product. Since it has a strong tendency to take up water, it was dried in a vacuum over phosphorus pentoxide and was then used without further purification. For convenience in handling, it was made up into pellets, which were again dried over phosphorus pentoxide in vacuum before introducing into the cell. These pellets weighed from 0.1 to 0.50 g.

The density of the bromine solution of trimethylammonium chloride decreases with increasing concentration. It was, therefore, necessary to determine this change in density. A Westphal balance was employed using a heavier bob than the one furnished, since the former would not sink in the bromine. This made a calibration necessary which was obtained by making another determination of the density of pure bromine, using a pycnometer consisting of a glass bulb of 21 cc. capacity and having a stem of 1 mm. diameter. The instrument was calibrated with water in the usual way, and the ratio of the two values found for the density of bromine was taken as the calibration correction of the balance. At 18° the weight of water was found to be 21.3953 g., the weight of bromine 67.0458 g. In making the density determinations with the balance it was found necessary to suspend the bob by a platinum wire about one meter in length in order that the balance might not be attacked by the bromine vapors. The densities are given below. Concentrations, expressed in mols of salt per liter of solution, are given in the first column, the densities in the second, and the concentration expressed in mols of bromine per mol of salt in the third. Within the limits of error the density is a linear function of the fractional concentration.

TABLE II.

Concentration.	Density.	Mols of bromine per mol of salt.
0.00 (pure bromine)	3.134	..
0.5923	3.073	141.3
0.9237	3.06	90.78
1.917	2.956	44.12

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Procedure.—The method followed in making up the solutions was to weigh the amount of bromine introduced into the cell and then to add the weighed pellets of salt. In this way the concentration was gradually increased from the most dilute to the most concentrated solution.

The salt went into solution very readily, most of it dissolving in the course of a half hour. A slight shaking, which the bent neck of the cell made very simple, served to get the remainder of the salt into solution.

Experimental Results.—In Table III are given the results of three independent series of measurements. All measurements were made at 18.00°. No correction was made for the conductance of the solvent.

TABLE III.

	Temperature 18° ± 0.01°.					Cell constant 0.1950.		
No.	Weight, salt, g.	Conc.	Resistance.	$L \times 10^4$.	A.	Log V.	Log (cA).	Log (cA^2).
			Run No. 1, 73.07 g. of Bromine.					
1....	0.2027	0.09076	6,399.0	0.3893	0.3186	1.042	2.4611	3.9644
2....	0.4115	0.1843	618.2	3.992	1.624	0.736	1.4702	1.6886
3....	0.6160	0.2750	215.5	8.580	3.121	0.5608	1.9334	0.4227
4....	0.8156	0.3800	114.5	16.14	4.346	0.4304	0.2077	0.8457
5....	1.2447	0.5520	49.44	37.32	6.761	0.2581	0.5719	1.4020
6....	1.6560	0.7320	29.65	62.09	8.484	0.1355	0.7930	1.7213
7....	2.0401	0.8910	21.24	86.52	9.699	0.0460	0.9371	1.9238
8....	2.4427	1.0665	16.12	113.8	10.43	1.9720	1.0561	2.0843
9....	2.8401	1.2356	13.04	141.9	11.49	1.9073	1.1520	2.2122
			Run No. 2, 116.05 g. of Bromine.					
1....	0.1029	0.029	252,300.0	0.007334	0.02529	1.5376	4.8653	5.2682
2....	0.2104	0.0595	30,061.0	0.06115	0.1038	1.2269	3.7892	4.8054
3....	0.3404	0.0954	4,971.0	0.3722	0.3880	1.0421	2.5708	2.15962
4....	0.4539	0.1285	1,809.0	1.023	0.7945	0.8900	1.0098	2.90992
5....	0.5646	0.1592	922.1	2.006	1.261	0.7892	1.3024	1.4031
6....	0.7423	0.2093	428.6	4.316	2.063	0.6794	1.6351	1.9496
7....	0.9320	0.2618	241.1	7.669	2.929	0.4817	1.8847	0.3515
8....	1.1106	0.3110	161.5	11.44	3.683	0.5072	0.0587	0.6247
9....	5.259	0.3427	82.25	22.45	5.259	0.3688	0.3513	1.0713
10....	6.469	0.5334	53.59	34.50	6.469	0.2730	0.5378	1.3438
11....	8.008	0.6887	33.46	55.07	8.008	0.1630	0.7409	1.6444
12....	9.865	0.9323	19.99	98.65	9.865	0.0302	0.9636	1.9577
			Run No. 3, 54.72 g. of Bromine.					
1....	0.9937	0.4944	43.77	42.18	8.531	0.2059	0.6250	1.5561
2....	1.1297	0.5599	29.86	51.3	9.163	0.1519	0.7101	1.6717
3....	1.7316	0.8546	15.90	115.4	10.73	1.9968	1.0623	2.1929
4....	2.2742	1.314	10.94	157.0	11.00	1.9814	1.2227	2.3258

At the head of the table is given the weight of bromine in the cell. In the first column is given the number of the observation, in the second the weight of the salt, in the third the concentration is given in gram equivalents per liter, in the fourth the resistance of the solution, corrected for the resistance of the leads, 0.14 ohm; in the fifth column is given the

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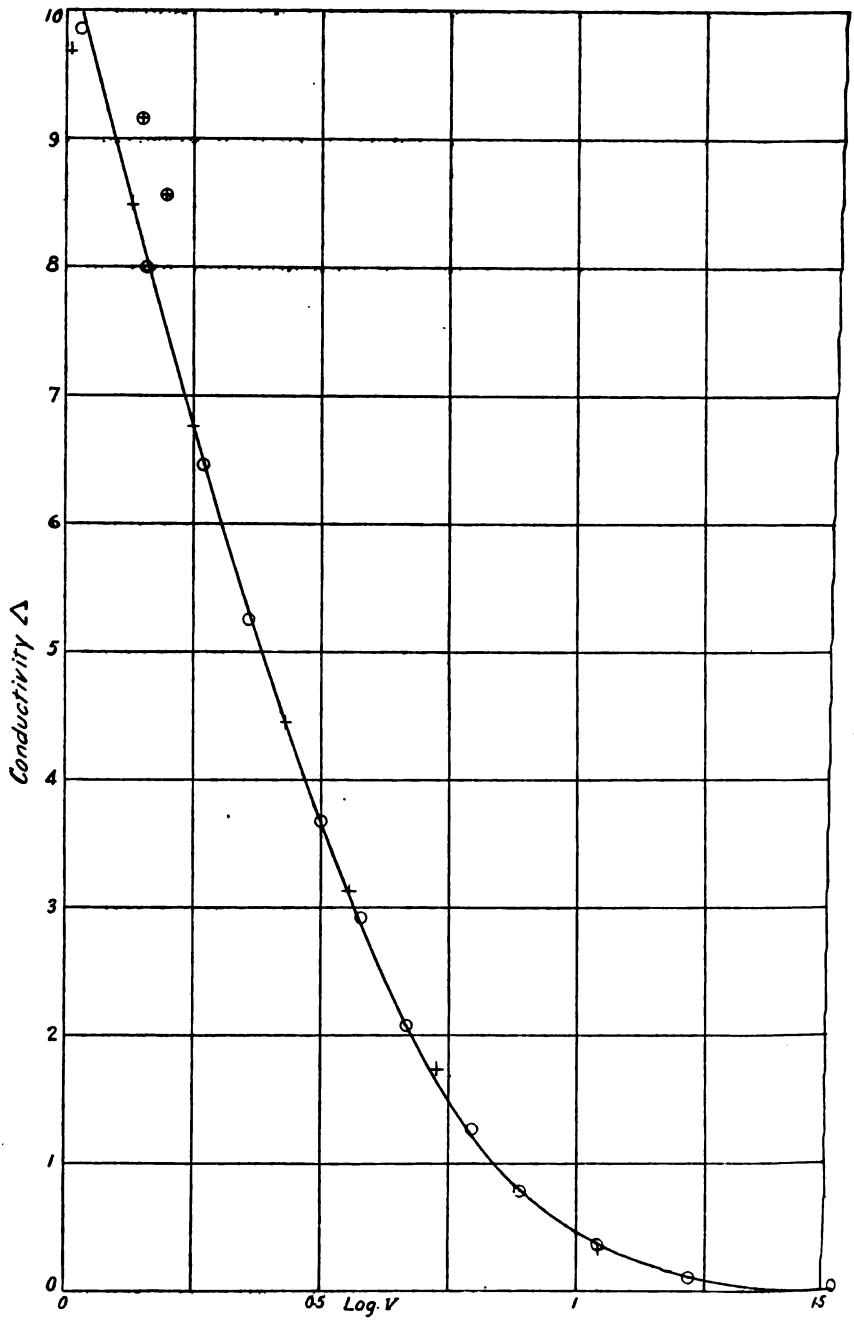

Fig. 1.—Conductance-concentration curves. Trimethylammonium chloride in bromine.

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specific conductance L of the solution multipled by ten, the equivalent conductance Λ is given in the sixth, the logarithm of the dilution V in liters per equivalent is given in the seventh column, and in the eighth and ninth columns are given log ($c\Lambda$) and log ($c\Lambda^2$), respectively.

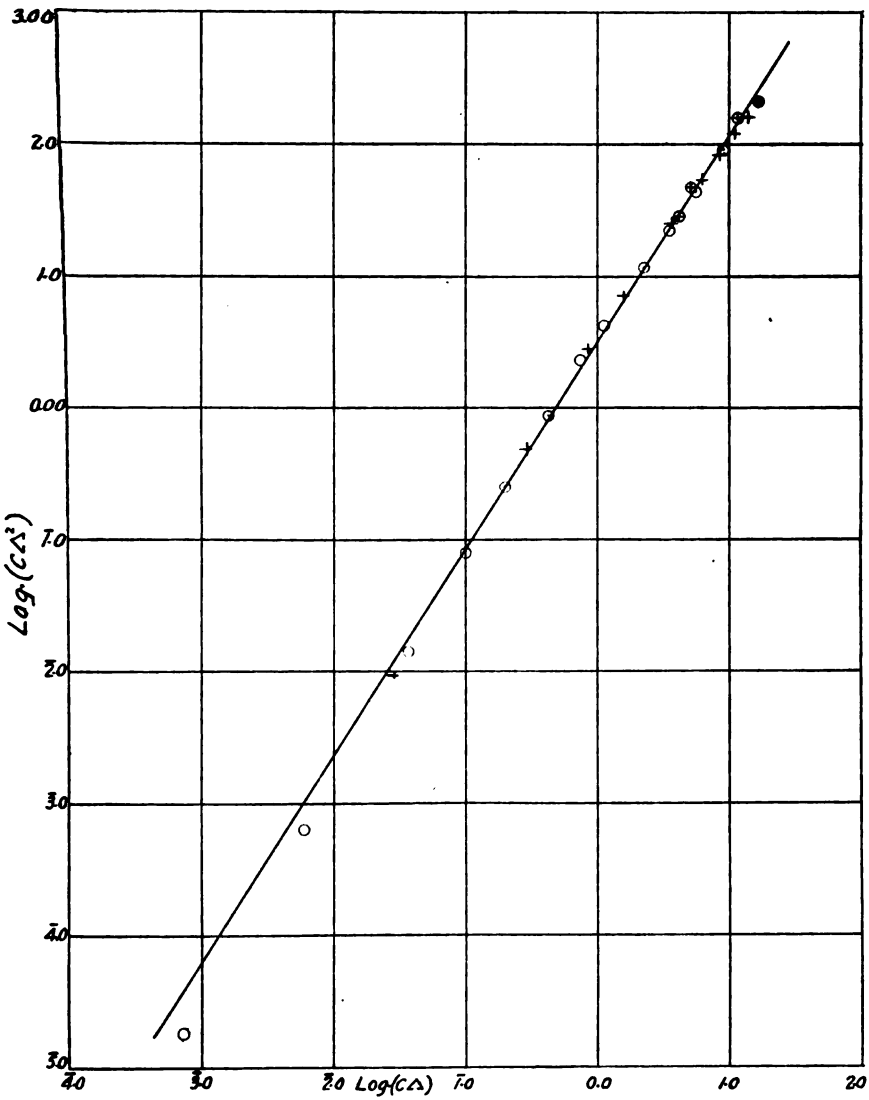

Fig. 2.—m-P plot for solutions of trimethylammonium chloride in bromine.

Discussion.—The results are shown graphically in Figs. 1, 2 and 3. In Fig. 1, values of Λ are plotted against log V, Fig. 2 is an M-P plot,[1] values

[1] Kraus and Bray, THIS JOURNAL, 35, 1324 (1913).

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of log ($c\Lambda$) being plotted against those of log ($c\Lambda^2$). As is generally the case with solutions in solvents of low dielectric constant, there is no tendency for the conductance to rise with increasing values of V. That is, the conductance curve continues to drop as the dilution increases. This

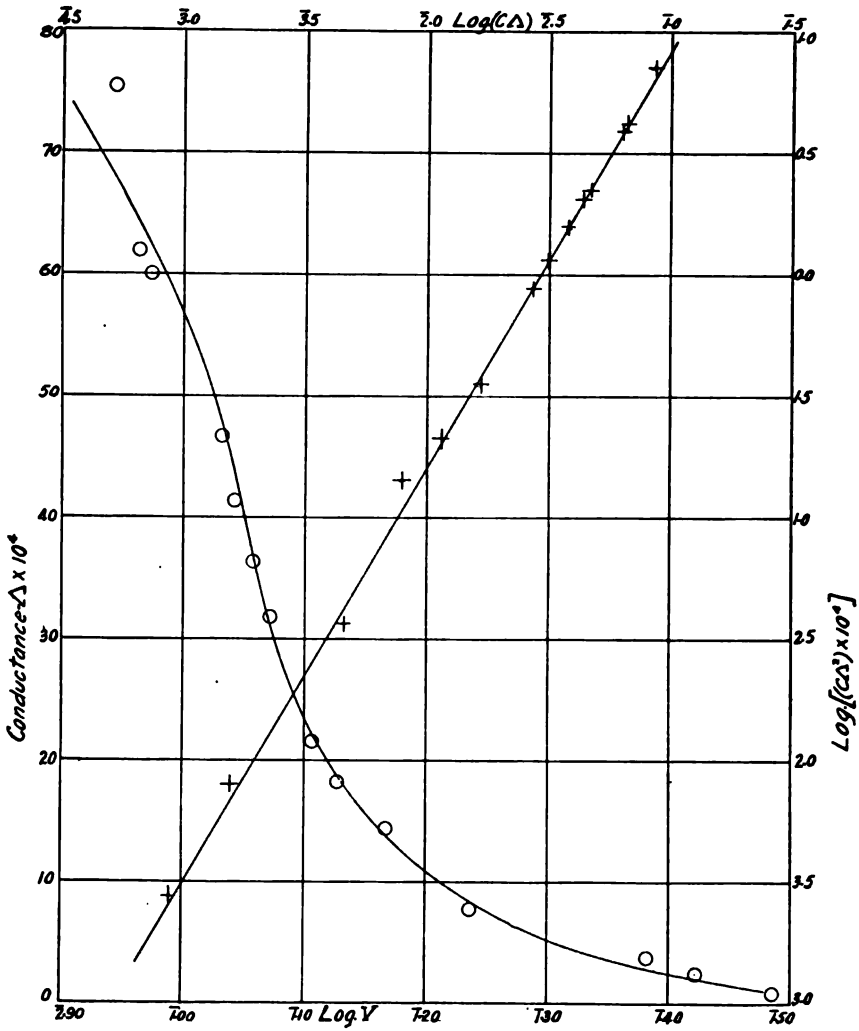

Fig. 3.—m-P and conductance-concentration plot. Iodine and bromine.

is in contrast to the behavior of the ordinary solutions in solvents of moderately high dielectric constant in which there is a minimum in the conductance curve with a marked rise at higher dilution.

The values of Λ increase less rapidly at higher ion concentrations. This is a characteristic phenomenon of conducting solutions in general and is doubtless due to the rapid increase in the viscosity of the solution.

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The m-P plot (Fig. 2) shows that the solution conforms to the equation of Kraus and Bray. Even in the most dilute solutions, whose resistance was about 250,000 ohms, the points conform reasonably well to a straight line.

From the plot, the values of the constants m and P may be determined giving

$$\log (c\Lambda^2) = 1.62 \log (c\Lambda) + \log 0.55.$$

If Λ_0 is known, the value of D in the general equation may be determined from the equation

$$D = P/\Lambda_0^{2-m}.$$

Λ_0 cannot be directly determined, but Λ_0 is approximately a linear function of the fluidity of the solvent. We may then determine Λ_0 from the equation

$$\Lambda_0 = Kf,$$

where f is the fluidity and $K = 0.517$ (approximately). The viscosity of bromine at the temperature used is 0.010. This gives $\Lambda_0 = 51.7$. With this value of Λ_0 we obtain $D = 0.849$. This value of D is higher than that of most solvents. It may be that for solvents of very low dielectric constant the value of D rises. On the other hand, it may be that the mobility of the ions is not correctly given by the equation assumed above.

In order to have a basis of comparison, Plotnikow's results in the case of solutions of iodine in bromine were also examined. The method of procedure was similar to that used above.

These values are plotted in Fig. 3. The values of m, P and D are obtained in the same way as for trimethylammonium chloride and are as follows: $m = 1.7354$; $P = 0.048$; $D = 0.1691$.

In Fig. 3 are also plotted values of log V against Λ. The rise in conductance with increasing concentration is very much smaller than it is in the case of trimethylammonium chloride. It should be noted than the concentrations in the case of solutions of iodine in bromine are much larger than those of trimethylammonium chloride. It would seem to show that, when viscosity effects are not too great, the equation applies to very high concentrations.

The other substances with which Plotnikow worked hardly afford a basis of comparison. He found that, while a few metallic bromides are soluble in bromide, for example, aluminium bromide, they do not give conducting solutions. Antimony bromide gave a solution of very slight conducting power. Only phosphorus pentabromide gave a solution having an appreciable conductance and then only in very concentrated solutions.

Summary.—The conductance of a typical electrolyte in bromine has been measured.

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The conductance values were found to be greater than those of any of the compounds studied by Plotnikow, none of which are typical electrolytes.

The values of m and D for trimethylammonium chloride are in fair agreement with those usually found for solutions in different solvents.

The conductance follows the dilution equation of Kraus and Bray.

WORCESTER, MASS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

A PRELIMINARY STUDY OF REVERSIBLE REACTIONS OF SULFUR COMPOUNDS.

BY GILBERT N. LEWIS, MERLE RANDALL AND F. RUSSELL V. BICHOWSKY.

Received October 16, 1917.

Before publishing the details of a number of investigations which have extended over a period of eight years and which have finally permitted the calculation of the free energy of important sulfur compounds, we shall discuss briefly the nature and difficulties of the problem, and shall describe a large number of preliminary experiments. Designed as a means of orientation, these experiments were for the most part rough and qualitative. Some were selected for extensive quantitative investigation, and of these a few led to the successful results to be described later. They all help to throw light upon the extremely complicated behavior of sulfur compounds.

Sulfur is an element which appears in so many various types of compounds, in which it displays different valences, that the difficulty in obtaining data suitable for free energy calculations is due not to the paucity but to the wealth of reversible reactions. Indeed here, as with the nitrogen compounds, it is hard to find a reversible reaction which is not attended by numerous side reactions.

In studying the oxygen compounds of sulfur, the first important substance to consider is sulfur dioxide. Its free energy could be determined most directly from measurements of its thermal dissociation. Deville[1] passed sulfur dioxide through a "hot-cold" tube, and found evidence of a slight dissociation at 1200° C. We have, however, repeated these experiments between 1000 and 1500° and found, even at the highest temperatures, that the dissociation is too small to furnish a reliable method for obtaining the free energy of formation.

Turning, therefore, to a more complicated system, we have studied equilibria is *systems* containing sulfur, oxygen and hydrogen. *This system*, under varying conditions, yields, besides hydrogen and oxygen, gaseous S_8, S_6, S_2, S, the numerous solid and liquid forms of sulfur, steam,

[1] Deville, *Ann. chim.*, 145, 94 (1865).

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hydrogen sulfide, sulfur dioxide, sulfur trioxide, sulfuric acid vapor, and, in the presence of liquid water, sulfurous acid, sulfuric acid, and numerous thionic acids. We have, however, studied this system at the boiling point of sulfur, where sulfur and water vapor react to form small amounts of hydrogen sulfide and sulfur dioxide, without any disturbing side reaction, and between 900 and 1400°, where the only substances present in large amount are hydrogen, sulfur as S_2, hydrogen sulfide, steam and sulfur dioxide. These investigations are described in detail in the following papers.

In place of sulfur, silver sulfide was treated with water vapor at high temperatures, and since large amounts of hydrogen sulfide and sulfur dioxide were at first obtained, a somewhat extensive investigation of the equilibria in this reaction was undertaken, but had to be abandoned when it was discovered that the silver sulfide which was employed, and which was ostensibly of the highest purity, contained an excess of sulfur. When this excess was removed the reaction took place to no measurable extent up to 800°, where other phases besides pure solid silver and silver sulfide appear.

Sulfur as a Reducing Agent.—At room temperatures sulfur is not a highly reactive substance. In at least one case it is known to act as an oxidizing agent. The reaction

$$S + 2HI = H_2S + I_2$$

has been investigated, and furnishes one of the methods by which the free energy of formation of hydrogen sulfide has been obtained. As a reducing agent sulfur becomes noticeably reactive between 100° and 200°, as shown by the following experiments in aqueous solutions, carried out in evacuated and sealed glass or quartz tubes, heated for some hours to about 160°.

Cations whose sulfides are insoluble in strong acids, such as silver, mercurous, cupric, bismuth, lead, were slowly but quantitatively precipitated as sulfides.[1] Oxidizing cations such as mercuric, ferric, stannic, were quantitatively reduced.

The anions, nitrate, permanganate, iodate, bromate, were reduced to nitric oxide, manganese dioxide, iodine, bromine, respectively. Two days' heating at 180° showed no reduction of sulfates, periodates, or perchlorates. Chlorates appeared to be very slowly reduced. It seems at first paradoxical that in solutions in which reduction by sulfur occurred a strong test for hydrogen sulfide was usually obtained. This seems to indicate that the reaction

$$2H_2O + 3S = 2H_2S + SO_2,$$

[1] Cf. Geitner, *Pharm. Ann.*, 129, 350 (1864); Filhol and Senderens, *Compt. rend.*, 94, 152 (1881); *Ber.*, 14, 2415 (1881).

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is the primary reaction and that the sulfur dioxide thus produced (existing in solution not chiefly as such but in the form of thionic acids) is the reducing agent. Even after heating sulfur with pure water or dilute irreducible acids the odor of hydrogen sulfide is very noticeable,[1] but no test for sulfur dioxide could be obtained, nor did any of the recognized tests for thionic acids give positive results. The failure of these tests does not, however, show conclusively the absence of thionates in small amounts.[2]

Although we are therefore unable to state the composition of the solution obtained by heating sulfur and water, an interesting observation was made which bears upon this question. When sulfur is heated in quartz with dilute neutral or slightly alkaline solutions of non-reacting salts such as potassium chloride, sodium sulfate, magnesium sulfate or tripotassium phosphate, a blue color of the shade of indigo appears, and is first noticeable, in a tube of 0.5 cm. diameter, at about 130°. The intensity of the color increases rapidly with the temperature. On cooling, the color disappears and milky sulfur is precipitated. Pure water in quartz gives no color with sulfur, but in glass the color appears, owing doubtless to the dissolved alkali. In the presence of acid this color does not appear. We find that this colored solution was described by Geitner[3] in 1864, but no satisfactory explanation has been given. The fact that the color is inhibited by acid indicates that it is not due to an elementary molecular species of sulfur, but to some compound formed by interaction with the solvent or with hydroxyl ion. The close analogy between water and ammonia as solvents indicates that the colored solutions of sulfur in water and those discovered by Moissan[4] in liquid ammonia are to be similarly explained. In fact we have found that under certain circumstances sulfur solutions in liquid ammonia are rendered colorless by a substance which is an acid in that solvent, namely ammonium chloride. Colored solutions of sulfur in sulfur trioxide,[5] boron oxide,[6] phosphorous pentoxide, potassium thiocyanate,[6] potassium cyanide,[6] glycerine,[7] ethyl alcohol,[8] and acetone,[8] have been found.

The Reduction of Sulfuric Acid by Sulfur.—The apparently mysterious

[1] The action of sulfur on water and the formation of H_2S has also been studied by Gerard, *Compt. rend.*, **56**, 797 (1863); Gelis, *Ann. Pharm.*, **129**, 350 (1864); *Compt. rend.*, **56**, 1014 (1864); Cross and Higgins, *J. Chem. Soc.*, **35**, 249 (1879); *Ber.*, **12**, 846 (1879); Geitner, *Loc. cit.*

[2] Takamatsu and Smith, *J. Chem. Soc.*, **37**, 608 (1880).

[3] Geitner, *Loc. cit.*, see also Colson, *Bull. soc. chim.*, [2] **34**, 66 (1880); Senderens, *Ibid.*, [3] **6**, 80 (1891).

[4] Moissan, *Compt. rend.*, **132**, 510 (1901).

[5] Discovered by Buchholz, Gehlen's *Neues J. Chem.*, **3**, 7 (1804); see Gmelin Kraut, "Handbuch," Heidelberg, **1**, 1, 436 (1907).

[6] Hoffman, *Z. Chem. Ind. Kolloid*, **10**, 275 (1912).

[7] Hoffman, *Loc. cit.*; also *Z. angew. Chem.*, **19**, 1089 (1909).

[8] Paterno and Mazzucchelli, *Atti Accad. Lincei*, [1] **16**, 465 (1907).

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disappearance of sulfur dioxide in the experiments just mentioned, which is even more striking in other experiments which we shall discuss shortly, was explained by the discovery of a reaction which, although mentioned by Preistley in 1775 and re-discovered by numerous investigators,[1] is at present little known. In sealed tubes containing sulfur dioxide and water and heated to about 150°, sulfur is formed at a noticeable rate according to the reaction

$$3SO_2 + 2H_2O = S + 2H_2SO_4.$$

The reverse of this reaction can be readily obtained by heating sulfur with sulfuric acid, and this evidence of the reversibility of the reaction led to a study of the equilibrium in the reduction of concentrated sulfuric acid by sulfur. The result of the investigation will be given in a later paper.

The Reduction of Carbon Dioxide by Sulfur.—One of the most direct methods of determining the free energy of formation of sulfur dioxide would be the study of the equilibrium in the reaction

$$S + 2CO_2 = SO_2 + 2CO.$$

As a preliminary to this investigation, Lewis and Lacey[2] studied the equilibrium between carbonyl sulfide, carbon monoxide and sulfur. Further work in this direction was discontinued when it was learned that similar experiments were being carried on in the Geophysical Laboratory of the Carnegie Institution. This work has just been brought to a successful conclusion,[3] and the results obtained will later afford us one of the most important methods of determining the free energy of sulfur dioxide.

The Reduction of Sulfates.—We have just spoken of the reduction of H_2SO_4 by sulfur. We shall consider now certain other reactions which show the action of other reducing agents upon sulfates and sulfate ion.

Solid sulfates are reduced by hydrogen gas at moderate temperatures. Hydrogen was passed over sodium sulfate at 220–250°. The gas emerging gave a marked test for hydrogen sulfide with lead acetate, and deposited elementary sulfur. The residue was distinctly alkaline and contained no sulfide. At 300° silver sulfate is similarly reduced, the reaction being obviously complex. The issuing gas gave fumes and smelled strongly of sulfur dioxide. At the end of about an hour the silver sulfate was com-

[1] Berthelot, *Mem. l'Acad.*, **1872**, 599; Fourcroy and Vacquelin, *Ann. chim.*, **24**, 234; Geitner, *Ann.*, **129**, 140 (1864); Hautefeuilles, *Bull. soc. chim.*, [2] **7**, 1867; Tyndall, *Chem. News*, **18**, 266 (1868); Morreu, *Compt. rend.*, **69**, 397 (1869); Walden and Centnerszwer, *Z. physik. Chem.*, **42**, 432 (1902); Sainte Pierre, *Compt. rend.*, **74**, 52 (1872); Jungfleisch and Brunel, *Ibid.*, **156**, 1719 (1913); **157**, 257 (1913); Berthelot, *Compt. rend.*, **96**, 298 (1883).

In spite of this rather extensive reference list this reaction is little known, Berthelot, Fourcroy and Vacquelin, Geitner and Sainte Pierre were each apparently unaware of the older work on the subject.

[2] Lewis and Lacey, THIS JOURNAL, **37**, 1976 (1915).

[3] Ferguson, *Proc. Nat. Acad. Sci.*, **3**, 371 (1917).

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pletely destroyed and the residue, though black in color, was doubtless chiefly metallic silver, and dissolved in dilute nitric acid. Thallous sulfate at a somewhat higher temperature was also reduced by hydrogen. The gas gave a copious white precipitate with lead acetate, this precipitate being soluble in dilute nitric acid, showing that in this case sulfur dioxide was produced but no hydrogen sulfide. At lower temperatures (about 150°) sulfate ion in aqueous solution is reduced even by mild reducing agents. These miscellaneous experiments on the reduction of sulfates were discontinued in favor of the two reversible reactions which will be discussed in later papers, namely, the reduction of sulfuric acid by sulfur and by mercury.

Potential of the Sulfur Dioxide Electrode.—Instead of reducing sulfuric acid by a chemical agent, the reduction may be made by the aid of the electric current, and we shall describe in this section unpublished experiments made in connection with this investigation by the late Arthur Edgar[1] with the purpose of testing the reversibility of a sulfur dioxide–sulfate-ion electrode. An iridized platinum electrode over which bubbled sulfur dioxide (diluted with air) was used in a solution of sulfuric acid. The other electrode was of mercury covered with mercurous sulfate in the same acid. This cell was measured at 25° with a view of determining the free energy of the reaction

$$SO_2 + Hg_2SO_4 + 2H_2O = 2H_2SO_4 + 2Hg.$$

The cell so constituted behaved in a fairly satisfactory manner. Equilibrium conditions apparently were not reached with great rapidity, but, upon standing, steady values were obtained reproducible to within about a millivolt.

TABLE I.

Electromotive Force of the Cell Pt, SO_2, H_2SO_4, Hg_2SO_4, Hg.

Mol % H_2SO_4.	Pressure of SO_2 in atmospheres.	E. M. F.	E. M. F. calculated $[SO_2] = 1$ atm.
0.09555	0.01328	0.301	0.356
0.09555	0.00689	0.295	0.358
0.8946	0.1091	0.274	0.302
0.8946	0.05080	0.266	0.305
0.8946	0.02479	0.259	0.306
0.8946	0.01328	0.251	0.306
0.8946	0.00689	0.238	0.302
0.915	0.969	0.324	0.324
0.915	0.969	0.324	0.324
4.618	0.02489	0.200	0.247
4.618	0.01333	0.192	0.247
10.303	0.9814	0.189	0.189

[1] These experiments were made in the Research Laboratory of Physical Chemistry of the Mass. Institute of Technology.

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In Table I are given results with several concentrations of sulfuric acid and with a wide variation in the partial pressure of sulfur dioxide. If the e. m. f. is a measure of the free energy of the above reaction, we should have the equation

$$E = E^\circ - \frac{RT}{2F} \ln \frac{(H_2SO_4)^2}{[SO_2]\,(H_2O)^2}$$

where $[SO_2]$ represents the pressure of sulfur dioxide and the terms in parenthesis represent not the concentrations but the corrected concentrations or activities of sulfuric acid and water. In as far as the effect of the pressure of the sulfur dioxide is concerned, the equation is verified as shown in the last column of the table, and this would also tend to establish the reversibility of the electrode. But when we consider the effect of change of concentration of sulfuric acid, we find the change of e. m. f. with the concentration is only about one-half what it should be according to the equation. The activities of water and of sulfuric acid used in this calculation were obtained from the measurements made by Brönsted[1] and by Dolezalek[2] and also by Edgar upon the e. m. f. of the cells H_2, H_2SO_4, Hg_2SO_4, Hg and Pb, $PbSO_4$, H_2SO_4, $PbSO_4$, PbO_2. The former cell has also been subjected to a more exact investigation by Randall and Cushman and their work will form a part of this series of papers. There can be no question that the e. m. f. equation given above fails. We have at present no explanation to offer for this result, except that the cell does not give reversibly the reaction under consideration.

Reactions Involving Silver Sulfite.—In the early stages of our investigation we hoped that important results might be obtained from a study of reversible reactions of silver sulfite, especially the two reactions

$$Ag_2SO_3 = Ag_2O + SO_2.$$
$$2Ag_2SO_3 = 2Ag + Ag_2SO_4 + SO_2.$$

Pure, dry silver sulfite was heated in a bath of boiling carbon tetrachloride at 76°. It was contained in a glass tube connecting outside the bath with a closed manometer. Sulfur dioxide was evolved until its pressure was equal to the vapor pressure of liquid sulfur dioxide, and drops of the liquid condensed in the manometer. In another experiment we actually found liquid sulfur dioxide in that part of the tube heated to 76°. The reaction is sluggish, but there may be a true equilibrium pressure not far from that of liquid sulfur dioxide at the same temperature. The experiments, however, were discontinued when it appeared that the solid phase produced in the reaction is not silver oxide but rather a basic salt or solid solution. Indeed when silver sulfite was heated at atmospheric pressure to 140°, only about one-third of the theo-

[1] Brönsted, *Z. physik. Chem.*, **68**, 703 (1909).
[2] Dolezalek, *Z. Electrochem.*, **4**, 349 (1898).

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retical amount of sulfur dioxide was evolved, and the mixture may be heated to fusion without much further loss of sulfur dioxide.

A more rapid reaction occurs according to the second of the above equations when silver sulfite is heated in the presence of water.[1] It is evident that in the reaction as written the water can take no part except as a catalyzer. When a mixture of silver sulfite and water was heated to 110° in a tube connecting with a manometer, the partial pressure of sulfur dioxide reached 4 atmos. But when the tube was heated to 132° this partial pressure fell to less than 3 atmos. This surprising result was not understood until further investigation showed that when the system is heated at constant temperature the pressure rises rapidly to a maximum and then falls off, apparently without limit, according to the law of a monomolecular reaction. This effect is in all probability due to the simultaneous occurrence of two independent reactions, the first of which we have no reason to doubt is the one written above. The second reaction we believe to be

$$Ag_2SO_4 + SO_2 + 2H_2O = 2Ag + 2H_2SO_4.$$

In fact an analysis of the mixture showed the presence of sulfuric acid. This reaction is quite analogous to the corresponding one with mercurous sulfate, which we shall discuss at length in another paper. It seems very likely that it might be possible to separate these two reactions and obtain true equilibrium conditions in the former, but we have not proceeded further in these directions.

The various reactions which have been chosen for detailed study will be discussed in other papers. In the present group will be included two papers on the reactions of sulfur dioxide, and one on the free energy of dilution of sulfuric acid, while in a later group, which we hope to publish in the near future, we shall include papers involving the free energy of formation of sulfuric acid and finally a general paper on the free energy of the sulfur compounds.

BERKELEY, CAL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

EQUILIBRIUM IN THE REACTION BETWEEN WATER AND SULFUR AT THE BOILING POINT OF SULFUR.[2]

BY GILBERT N. LEWIS AND MERLE RANDALL.

Received October 16, 1917.

The well-known reaction between gaseous hydrogen sulfide and sulfur dioxide to give sulfur and water has been studied by numerous investi-

[1] This reaction is mentioned in Abegg's Handbuch, I, 714.

[2] This work was carried out in the Research Laboratory of Physical Chemistry of the Massachusetts Institute of Technology, and concluded in 1910.

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gators,[1] and their work indicates the probable reversibility of the reaction. Preliminary experiments at about 500° showed this to be the case, the reaction $2H_2O + 3S = 2H_2S + SO_2$ occurring rapidly in either direction according to the conditions imposed. In fact the rapidity of the reaction precludes the use of the method of determining the equilibrium by rapidly cooling the reacting substances and analyzing. The only practicable method which suggested itself depends upon the fact that, owing to a change in the number of mols during the reaction, there should be a corresponding pressure change. If the experiments are made in the presence of an excess of liquid sulfur, the other substances being in the gaseous state, the pressure of the other substances would be increased by one-half if the water were completely converted into hydrogen sulfide and sulfur dioxide. Since, however, under the conditions of our experiments the fraction of water which reacts is small, we have been obliged to scrutinize with unusual caution every possible source of error in the pressure measurements.

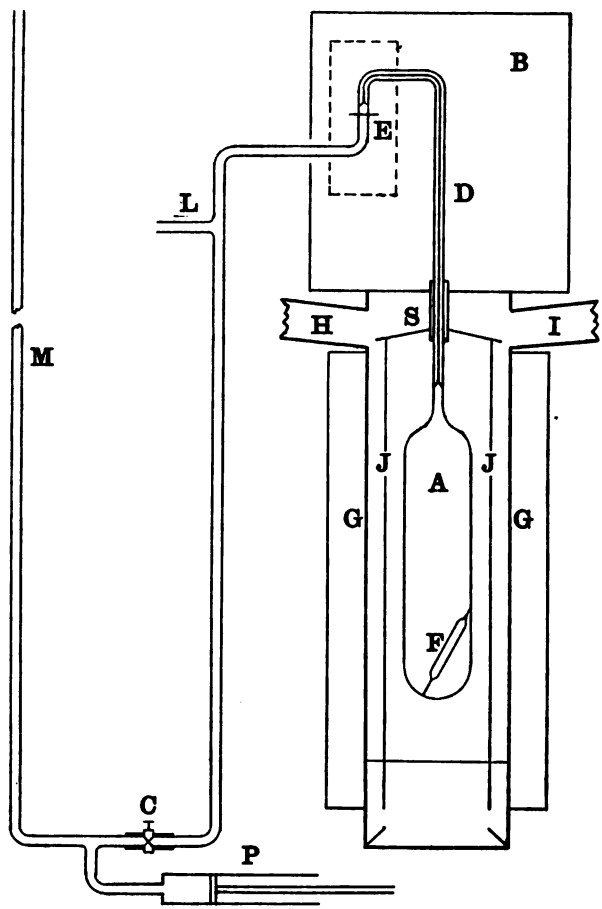

Fig. 1.

The apparatus (Fig. 1) consisted essentially of a glass reaction bulb, A, of about 175 cc. capacity, connected through the capillary tube D to the open manometer M. The level of the mercury in the short arm of the manometer could always be brought to the mark E, close to the end

[1] Mulder, *Jahresb.*, **1856**, 86; Corenwinder, *Compt. rend.*, **53**, 140 (1861); Gripon, *Ibid.*, **56**, 137 (1863); Meyers, *J. prakt. Chem.*, **108**, 123 (1869); Meyers, *Compt. rend.*, **74**, 195 (1872).

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of the capillary D, by means of the cylinder and piston P. The level of the mercury could be lowered and the tube A exhausted through the side tube L by means of a Toepler pump not shown in the figure. The screw clip C, operating on a small section of rubber tubing, served to control the flow of mercury in the manometer tubes during the adjustment of the pressures, but was always left open during the final readings.

The reaction tube A was heated by means of a bath of sulfur vapor. This vapor bath was made of a piece of steel pipe GG, 10 cm. in diameter and 48 cm. long, with a bottom piece welded in. Near the top two pieces of iron pipe H and I, about 2.5 cm. in diameter and 20 cm. long, were screwed in and served as condensers. These condenser tubes were given a slight grade. The top of the bath was turned off square in a lathe and was raised against an asbestos washer on the bottom of the sheet iron box B. A steel tube, JJ, about 6 cm. in diameter and flanged at the bottom, was held in the middle of the heater. The annular space between the tubes G and J formed a vapor jacket around the inner tube, inside which the reaction tube A was placed. The inverted mica cone S was fastened to the tube A by means of asbestos twine and prevented the cooler condensed sulfur from dripping upon this tube. The opening between the box B and the sulfur bath, through which the capillary D passed, was closed by a packing of asbestos cord. The sides of the bath were well jacketed with magnesia asbestos lagging. The bath was supported upon a heavy iron tripod, and heated by gas.

The sheet iron box B, lined with asbestos, and provided with a mica window in front of the reference mark E, surrounded the capillary D. The box was heated by two 100 watt lamps which served not only to keep the temperature of the box between 120° and 145° but also to illuminate the interior. The purpose of this box was to avoid condensation of water in the capillary.

A small thin-walled glass tube F was drawn down to a fine capillary at both ends, so as to have a volume of 0.04–0.06 cc. Boiled distilled water was then introduced and the ends so sealed that no air and a very small vapor space remained. The bulb would then explode when slightly heated. This bulb was weighed empty and after sealing.[1] The volume of the reaction tube A was determined by weighing the bulb empty, and filled with water. A weighed quantity, 2–4 g., of pure sulfur, in the form of a fine powder, was introduced into the tube with the sealed glass bulb containing the water. The reaction tube was then sealed to the capillary (D) and the cold vapor bath raised into its position beneath the box B. The level of the mercury was brought below L and the reaction tube exhausted. The connection to the pump was sealed off, and the level of

[1] A balance sensitive to 0.00003 g. was used. The mean of several readings was taken in each case.

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the mercury brought back to the reference mark E and the screw clip C closed.

The vapor bath was heated gradually, and then the lights in the box B were turned on.[1] As the temperature of the bath reached equilibrium, the height of the manometer was adjusted by manipulating the screw clip C and the piston P so as to keep the mercury at the reference point E. When the pressure in the bulb A had reached equilibrium, the barometric height was noted and the height of the mercury column in M above the reference mark E was determined.

Owing to the difficulty of the manipulations, a number of experiments were fruitless, but satisfactory measurements were made in six experiments, and the results are given in Table I. The first two columns give the weight in g. of water and of sulfur, the third gives the corrected volume of the reaction tube. The corrections include the expansion of glass, the volume of the sulfur left unvolatilized, of the fragments of the glass bulb which contained the water, and the volume of the capillary and connecting tube, which was always less than 0.1 cc. The fourth column gives the barometric pressure, and the last the observed pressure of the equilibrium mixture in millimeters.

TABLE I.

H_2O.	S.	Cor. vol.	Bar. Mm.	P.
0.04410	3.81	150.8	771	1554
0.05492	2.24	203.6	761	1476
0.05214	2.02	152.3	756	1656
0.05882	2.27	202.8	758	1538
0.04702	2.55	166.7	766	1519
0.05402	1.75	117.2	764	1978

Since the reaction chamber is surrounded by the vapor of boiling sulfur the vapor pressure of sulfur within the chamber should be identical with the barometric pressure. Therefore by subtracting the barometric pressure from the observed pressure we should be able to find the combined pressure of the three gases, steam, sulfur dioxide and hydrogen sulfide, and, by comparing this with the pressure calculated from the amount of water introduced, calculate the extent to which the reaction had occurred. Fortunately, before making this calculation it was decided to make certain incidental experiments which showed the existence of a small but appreciable error. First, experiments of the same character as those which we have described were made in the absence of sulfur. Two experiments of this type are reproduced in Table II in which the first column gives the weight of water introduced, the second the corrected volume of the bulb,

[1] These lights were turned on at such a time that the oven would come to about 130° a short time before the bulblet containing the water exploded. If the box B were heated for too long a time mercury would distil gradually into the tube D.

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the third the observed pressure, and the fourth the pressure which would be calculated from the gas law.

TABLE II.

H_2O.	Cor. vol.	$p_{obs.}$	$p_{calc.}$
0.05873	152.4	961	957
0.07781	183.2	1058	1055.5

The difference, which amounts to 4 mm. in the first case and 2.5 mm. in the second, seemed larger than could be accounted for at this temperature by a deviation from the gas law. This suggested the possibility that the excess pressure was due to adsorbed water which remained upon the surface of the reaction tube after prolonged exhaustion. This seemed the more likely, since it was impossible, owing to the conditions of the experiment, to heat the reaction tube during the preliminary exhaustion. This assumption was tested by another experiment in which neither water nor sulfur was put into the tube. A glass tube with a volume of 84 cc. was cleaned and washed as in the previous experiments, and after prolonged exhaustion as before, the pump was sealed off and the sulfur bath was raised into position and heated, the box B being left cold. The pressure rose at once to 5 mm. and remained constant as long as the heating was continued, but when the apparatus was cooled the pressure once more fell to zero. This seems to prove conclusively that there is enough adsorbed water upon the glass container to produce a pressure of several mm. at the boiling point of sulfur. The pressure in the experiment just described was greater than that deduced from the two experiments of Table II, since in this case a smaller glass tube was used, and the ratio of surface to volume was therefore larger.

This assumption of the existence of adsorbed water was further confirmed by two experiments in which sulfur, in sufficient amount to remain unvaporized at 445°, was heated in a tube of about 150 cc. in the absence of water. However, the sulfur could not be heated alone in the apparatus for it would then pass into the capillary tube and condense, or react with the mercury. For this reason a small amount of air was left in the tube to prevent the rapid diffusion of sulfur into the capillary. In the first column of Table III is given the initial pressure of the air, in the second the initial temperature, in the third the barometric pressure, in the fourth the observed pressure, and in the fifth the pressure calculated by adding to the barometric pressure the calculated pressure of the air. The transformation of some of the oxygen of the air into sulfur dioxide should not change the pressure, since one mol of oxygen gives one mol of sulfur dioxide.

TABLE III.

Init. press.	Init. temp.	Bar.	$p_{obs.}$	$p_{calc.}$
93	26	767	996	991
6.3	26	757	776.5	772

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Here again in the difference between the calculated and observed pressures we see the effect of the adsorbed water. These experiments show further that the sulfur itself gives off no appreciable amount of gas when heated.

In order to allow for the small effect of the adsorbed water, we have added 4 mm. to the calculated pressure of the water vapor in all of the experiments of Table I. We may now proceed to the final calculation of these results. In Table IV the first column gives the observed pressure, the second the partial pressure of the sulfur and of the water calculated from the gas law with the slight correction which we have just indicated. The third column gives the difference between Cols. 1 and 2. If this difference represents the extent of the reaction in which two mols of water disappear and two mols of hydrogen sulfide and one of sulfur dioxide are formed, it is equal to the partial pressure of sulfur dioxide and one-half the partial pressure of hydrogen sulfide. These are given in Cols. 3 and 4. The fifth column shows the barometric pressure, which is the partial pressure of sulfur vapor. The partial pressure of the water vapor is equal to the total pressure less the partial pressures of the other three gases. This is given in the sixth column. All these pressures have been given in millimeters, but it is customary to express the final value of the equilibrium constant in atmospheres. We have therefore reduced the values to this unit, and the seventh column gives the values of $K_p = [H_2S]^2[SO_2]/[H_2O]^2$.

TABLE IV.

$p_{obs.}$ Mm.	$p_{calc.}$ Mm.	p SO_2. Mm.	p H_2S. Mm.	p S. Mm.	p H_2O. Mm.	K_p. Atmos.
1554	1501	53	106	771	624	0.00201
1476	1435	41	82	761	592	0.00105
1656	1610	46	92	756	762	0.00088
1538	1483	55	110	758	615	0.00232
1519	1471	48	96	766	609	0.00157
1978	1913	65	130	764	1019	0.00139
					Mean,	0.00154

Considering the unusual magnification of the errors in obtaining K_p the results, which show an average deviation from the mean of 28%, may be regarded as quite satisfactory. We shall take as final value, the average, namely, $K_p = 0.00154$, and shall show in another paper how this value may be used in the calculation of the free energy of formation sulfur dioxide.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

EQUILIBRIUM IN THE REACTION BETWEEN WATER AND SULFUR AT HIGH TEMPERATURES. THE DISSOCIATION OF HYDROGEN SULFIDE.

BY MERLE RANDALL AND F. RUSSELL V. BICHOWSKY.

Received October 16, 1917.

The equilibrium in the reaction of water vapor and liquid sulfur to form gaseous hydrogen sulfide and sulfur dioxide has been determined by Lewis and Randall[1] at the boiling point of sulfur. It was extremely desirable to study this technically as well as theoretically important reaction under different conditions, especially at higher temperatures, both in order to make sure of the exact nature of the reaction and for the purpose of obtaining the equilibrium constant at a different temperature. But the method of Lewis and Randall possessed such inherent difficulties, and was so peculiarly adapted to a temperature in the immediate neighborhood of that at which it was employed, that it seemed expedient to look for some entirely new method of attack.

In order to determine the equilibrium in this reaction we must know, besides the initial composition and the equilibrium pressure of the mixture, the partial pressure at equilibrium of at least one of the substances involved. In the experiments of Lewis and Randall this substance was the sulfur vapor, the partial pressure of which was fixed at one atmosphere by having the equilibrium mixture in contact with an excess of liquid sulfur at its boiling point. They have also shown that the rapidity of the reaction[2] precludes the use of the method of determining the equilibrium by quickly cooling the reacting substances and analyzing. An attempt to fix the partial pressure of the sulfur by replacing the liquid sulfur by a solid substance, which had a constant determinable vapor pressure of sulfur, proved unsatisfactory. Water vapor was passed over pure silver sulfide[3] at a red heat, but it was found that the quantity of hydrogen

[1] Lewis and Randall, THIS JOURNAL, 40, 362 (1918).

[2] A mixture of moist SO_2 and H_2S, when passed through a clean glass tube at 60°, deposited but little sulfur. However, when the tube was etched sulfur was deposited rapidly at the same temperature. At temperatures above 200° the reaction was rapid in any case.

[3] Silver sulfide was supposed, on the basis of preliminary experiments, to give off considerable sulfur when heated with water vapor at red heat. However the C. P. Ag_2S which we used in these preliminary experiments was, apparently, a solid solution of Ag_2S and S; at least Ag_2S, which had been heated in a vacuum until partly decomposed, when treated with steam at 800° gave off very little S as H_2S and SO_2.

The apparatus which we used in the latter of these experiments is perhaps interesting. Since the yield is markedly dependent on the rate of flow, very slow and regular passage of the vapor is essential. This we secured by allowing the vapor to distil in vacuum through the furnace from one heated flask to another which was kept

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sulfide and sulfur dioxide, measured by the amount of total sulfur carried over, was too small for accurate measurement.

If the system studied by Lewis and Randall is investigated at temperatures in the neighborhood of 1000°, with sulfur vapor in place of liquid sulfur, then in addition to the four substances involved in their reaction a fifth substance is present, namely, hydrogen. If then any mixture of gases containing only hydrogen, sulfur and oxygen (in not too large amount) is heated to a high temperature, an equilibrium is established between the five gases, water, sulfur dioxide, hydrogen sulfide, hydrogen and sulfur. But since the equilibrium between hydrogen, sulfur and hydrogen sulfide is already known at different temperatures it still suffices, in order to determine completely the composition of the gases in equilibrium, to know the original composition of the gaseous mixture, the total pressure, and the partial pressure of any one of the five gases.

The reaction between hydrogen and sulfur dioxide is apparently slower than that between hydrogen sulfide and sulfur dioxide, so that when the hot gaseous mixture is suddenly cooled small amounts of hydrogen remain uncombined with an excess of sulfur. It seemed unlikely however that this method would prove adequate for the determination of the partial pressure of hydrogen in the equilibrium mixture.[1]

A similar problem was met by Loewenstein,[2] in his investigation of the dissociation of water vapor, and by Preuner,[3] and by Preuner and Schupp,[4] in their study of the dissociation of hydrogen sulfide. They allowed the equilibrium gases to come in contact with an evacuated platinum or palladium bulb heated to the equilibrium temperature. At the temperature used the rate of diffusion of the hydrogen was rapid, that of the other gases not appreciable. The total pressure of hydrogen inside the platinum bulb was taken equal to the partial pressure of the hydrogen in the mixture of gases. This method we have adopted in the present investigation.

The gas mixture containing a constant known percentage of oxygen, hydrogen and sulfur dioxide was prepared in the apparatus shown in Fig. 1, which consisted essentially of two wide U tubes R and S in which a 10% solution of potassium hydroxide was electrolyzed between platinum electrodes. The U tubes were joined, as shown, so that the oxygen (or hydrogen) from either or both the generators could be sent through the

at a slightly lower temperature. By regulating the temperature of the thermostats in which the two flasks were placed both the pressure and the rate of flow could be varied within wide limits.

[1] We were unable to use the excellent method of Langmuir (THIS JOURNAL, 28, 1357 (1906)) as the mixed gases reacted rapidly with the platinum wire.

[2] Loewenstein, *Z. physik. Chem.*, **54**, 715 (1906).

[3] Preuner, *Z. anorg. allgem. Chem.*, **55**, 279 (1907).

[4] Preuner and Schupp, *Z. physik. Chem.*, **68**, 157 (1909).

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sulfur burner EG, or directly into the furnace through Q, or to the atmosphere through N. A part of the oxygen was converted completely into sulfur dioxide by passing through the sulfur burner EG. This consisted of a large bulb filled with carbon-free sulfur which was kept boiling by allowing the tip of a quartz tube, F, heated to bright redness by passing a current through an enclosed coil of platinum wire, to dip under the surface

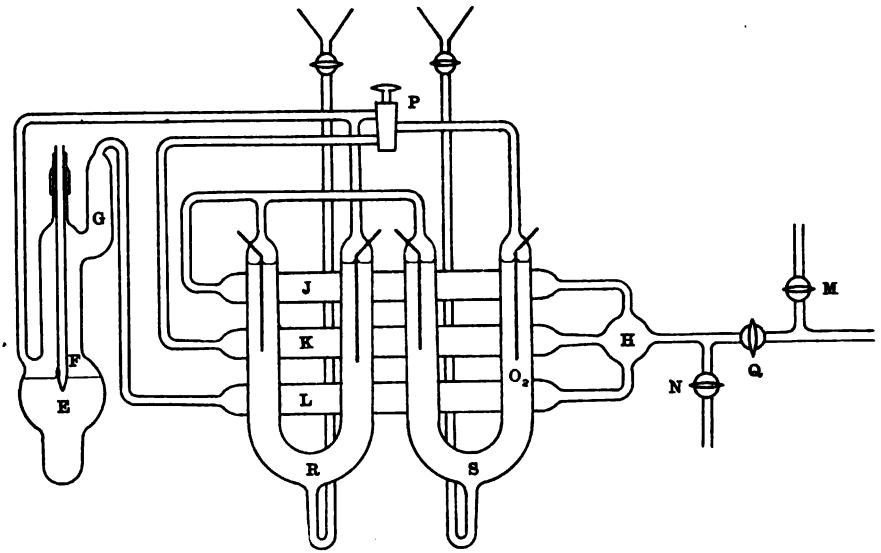

Fig. 1.—Apparatus for synthesizing a constant known mixture of O_2, H_2O and SO_2.

of the sulfur. The sulfur vapor and oxygen were superheated by the upper part of the heated quartz tube, and the oxygen burned completely to sulfur dioxide.[1] The boiling of the sulfur was regulated by raising or lowering F, and the excess of sulfur vapor which was always present was condensed in the wide outlet tube G which had a plug of glass wool in the upper end. The gases from the sulfur burner and the U tubes were severally dried over phosphorus pentoxide in tubes J, K, L, and mixed in the bulb H which was filled with glass wool.

The two U tubes were connected, in parallel, in series with a lamp bank to the regular direct current mains. Variations in the voltage did not affect the ratio of the currents in the two tubes, which ratio was kept at any desired values by means of adjustable resistances, and checked by a modified Wheatstone bridge with an accuracy of 0.1%. The composition of the gas entering the furnace was determined by the position of the stopcock P and these bridge ratios.

The reaction furnace and manometer for determining the pressure of hydrogen in the platinum bulb are shown in Fig. 2. The furnace B was

[1] The absorption by KOH in two experiments was 99.85% and 99.98%.

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simply a glazed porcelain tube (15 mm. inside diameter) wound with platinum wire and covered with an insulating cement. The plugs at the end were of the same cement. The gases were led into the reaction chamber through the quartz tube X, which was closely packed with platinum wire to prevent explosions, and the temperature was measured by the platinum platinum-rhodium thermocouple U connected to a sensitive potentiometer[1]

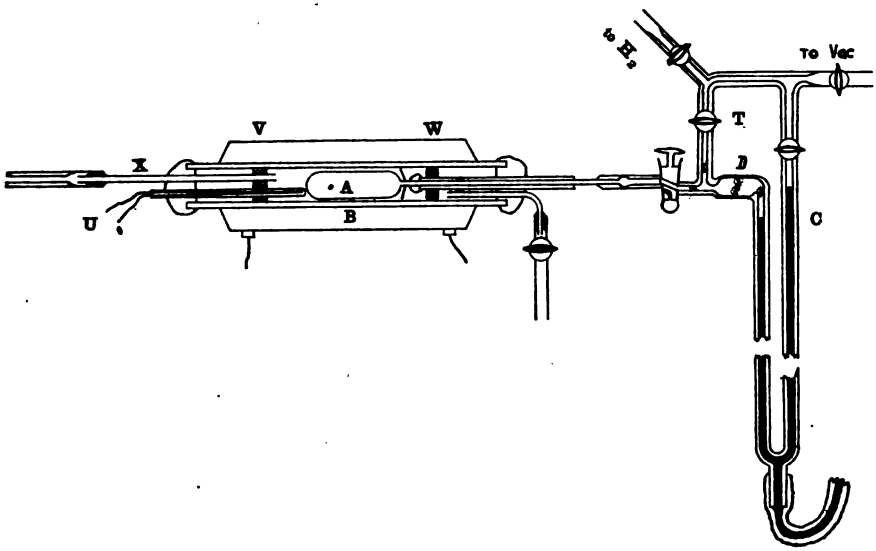

Fig. 2.—Reaction furnace and hydrogen manometer.

and carefully calibrated at 100°, 445° and 1062°. The thermocouple was contained in a thin-walled quartz tube. The diffusion bulb A was made of platinum, for we found that although palladium has theoretical advantages, it was extremely fragile when heated. The bulb was filled closely with small quartz rods in order to decrease the gas space, which must be filled by diffusion, as much as possible, and to prevent the bulb from collapsing when evacuated. The furnace space was made as small as possible to ensure uniform heating. The insulating cement was a good thermal conductor and helped to maintain uniform temperature conditions inside the furnace. To prevent radiation from the bulb to the ends of the furnace a series of bright platinum and transite baffles V and W were introduced. The cooler portions of the furnace were packed with coarse alundum powder to prevent diffusion. A quartz tube exit for the reacting gases was provided. The stem of the bulb A was made of very heavy-walled platinum capillary tubing and was protected through the temperature gradient by a porcelain tube which was cemented over it. The platinum tube was fused into the manometer C (2 mm. inside diam-

[1] Randall, Bichowsky and Rodebush, This Journal, 38, 1266 (1916).

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eter) which was compared with a standard barometer. Pure, dry hydrogen could be introduced from a side tube so that equilibrium could be approached from either direction. Vacuum stopcocks[1] were used throughout except in the generators (Fig. 1).

At the beginning of each experiment the tube F was brought to a bright red heat, the stopcock N opened, the stopcock Q closed, the bridge ratio adjusted, and the apparatus as far as Q swept out with a slow current of gas. The furnace was slowly heated to the required temperature and the tube A evacuated through T. Because of the somewhat rapid action of the sulfur gases on the platinum tube when heating or cooling, it was found advisable to heat and cool the tube in air and only expose it to the mixed gases from Q when heated. Under these conditions the tube was apparently unaffected.[2]

The evacuation of A was continued until no further residual gas was given off, as determined by cutting off the pump and noting the increase of pressure in C. The gas mixture was then introduced through X and the experiment allowed to proceed until the H_2 pressure in A was constant. The gas was then pumped out and pure, dry hydrogen introduced, from the reservoir not shown in the figure, until the pressure was slightly less than that of the original gas. When the pressure had again become constant the hydrogen was replaced by new hydrogen at a pressure slightly greater than equilibrium pressure. Thus the equilibrium was approached from both sides several times and the mean of the last two readings, which never differed by more than 1 to 2 mm. was taken.

In some earlier experiments there was a slight constant rate of diffusion or leak of other gases than hydrogen through the tube. In these cases the equilibrium pressure was estimated by plotting pressure against time and extrapolating back. Then the hydrogen pressure was made very slightly greater and less than this estimated value and the decrease or increase of pressure noted during the first minutes. The rate of leak was always very small and perfectly regular. The leak was eliminated in the last experiments by introducing a small drying tube (Fig. 2, D), filled with phosphorus pentoxide and potassium hydroxide, between the furnace and the manometer.

Our results are tabulated in Table I. The first column gives the absolute temperatures, Cols. 2 and 3 the ratios r and R defined by Equations 2 and 3, respectively (see below), Col. 4 the total pressure (barometric) in the furnace expressed in millimeters of mercury, Col. 5 the partial

[1] Randall and Bichowsky, This Journal, 37, 137 (1915).

[2] At low temperatures platinum, when heated in gases containing S, takes on a beautiful crystalline structure (due to PtS_2?) which, though destroyed at higher temperatures, apparently causes minute cracks, thus destroying the usefulness of the tube.

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pressure of hydrogen at equilibrium expressed in millimeters of mercury, and Cols. 6 and 7 the quantities in the two preceding columns expressed in atmospheres.

TABLE I.

T., abs.	r.	R.	P. Mm.	$[H_2]$. Mm.	P. Atmos.	$[H_2]$. Atmos.
1160	2	0.50	756	7.7	0.995	0.0101
1362	2	0.50	756	24.3	0.995	0.0319
1473	2	0.50	753	39.7	0.991	0.0521
1473	2	0.25	753	43.2	0.991	0.0566
1645	2	0.25	754	74.0	0.992	0.0972

Dissociation of Hydrogen Sulfide.—The measurements of Preuner and of Preuner and Schupp[1] on the dissociation of hydrogen sulfide did not extend above 1405°A. We have extended their measurements over the range from 1362°A to 1667°A. The excellent agreement between the two independent investigations enables us to put reasonable reliance upon not only these results but also upon those for the equilibrium between water and sulfur since the method is so nearly identical. The experiments were made directly in the apparatus shown in Fig. 2 in an identical manner with the previous measurements, except that hydrogen sulfide was introduced through M instead of the sulfur-water mixture.

Pure, dry hydrogen sulfide was prepared by heating calcium sulfide with a saturated solution of magnesium chloride to about 60°, and drying the slow stream of gas, which was given off, over phosphorus pentoxide. This very excellent method, first suggested by Habermann,[2] for the preparation of pure hydrogen sulfide, gives a very regular and easily controlled stream of gas. The rate of reaction is regulated by raising or lowering the temperature of the reaction flask, and the gas is probably purer than that prepared by any other method known.

The results are given in Table II, in which Col. 1 gives the absolute temperature, Col. 2 the total pressure (atmospheric) of the equilibrium mixture, Col. 3 the observed hydrogen pressure at equilibrium, Col. 4 the equilibrium constant $K_p = [H_2S]/[H_2][S_2]^{1/2}$ for the reaction $H_2 + {}^1/_2S_2 = H_2S$, and Col. 5 $\log K_p$.

TABLE II.

Temp., abs.	P. Mm.	$[H_2]$. Mm.	K_p. Atmos.	Log K_p.
1362	761	179	7.98	0.902
1473	761	235	4.39	0.643
1537	758	270	3.08	0.490
1667	758	325	1.81	0.257

The final values obtained by Preuner and Schupp[3] are given in Table III, in which the first row gives the absolute temperature and the second row the log of the equilibrium constant K_p calculated from their results.

[1] Preuner; Preuner and Schupp, *Loc. cit.*

[2] Habermann, *Chem. Zentr.*, [4] 2, 82 (1890).

[3] Preuner and Schupp, *Loc. cit.*

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TABLE III.

Temp., abs.	1023	1103	1218	1338	1405
Log K_p	2.025	1.710	1.305	0.964	0.793

These results will be discussed further in a later paper.

Calculation of the Partial Pressures in the Equilibrium between Water and Sulfur.—Five gases were present at equilibrium and the following five condition equations, solved simultaneously, enable us to calculate the partial pressures of each of the gases:

$$[H_2] + [S_2] + [H_2S] + [H_2O] + [SO_2] = P \qquad (1)$$

$$\frac{2[H_2] + 2[H_2O] + 2[H_2S]}{[H_2O] + 2[SO_2]} = r \qquad (2)$$

$$\frac{2[S_2] + [H_2S] + [SO_2]}{[H_2O] + 2[SO_2]} = R \qquad (3)$$

$$\frac{[H_2S]}{[H_2][S_2]^{1/2}} = K_{H_2S} \qquad (4)$$

$$[H_2] = x \qquad (5)$$

In the above equations the symbols in brackets represent the partial pressures of the several gases, P the total pressure (atmospheric) at equilibrium, r the ratio of total hydrogen to total oxygen determined from the composition of the initial gases, R the ratio of total sulfur to total oxygen, K_{H_2S} the equilibrium constant for the dissociation of hydrogen sulfide, and x the measured partial pressure of hydrogen.

Equations 1, 4 and 5 are obvious and require no comment. Equation 2 was arrived at in the following manner: All the hydrogen and oxygen generated in the apparatus (Fig. 1) was present in the equilibrium mixture. If these gases existed in the equilibrium mixture as hydrogen and oxygen, the ratio $[H_2]/[O_2] = r = 2$. Some of the hydrogen, however, changed to water and hydrogen sulfide and some of the oxygen to water and sulfur dioxide. For each mol of hydrogen at constant volume changed to water and hydrogen sulfide, and each mol of oxygen changed to sulfur dioxide there will be no change of pressure. For each mol of oxygen changed to water, however, the pressure will be doubled. If we take half the partial pressure of the water in the equilibrium mixture and clear the equation of fractions we may write $[H_2]/[O_2] = r$ in the form given in Equation 2.

In the first three experiments all and in the last two only one-half of the oxygen generated was passed through the sulfur burner EFG (Fig. 1). For each mol of sulfur gas burned to sulfur dioxide two mols of oxygen were used. Therefore $[S_2]/[O_2] = R = 0.50$ in the first three and 0.25 in the last two experiments. Proceeding as above we obtain the equation in the form given in Equation 3.

With the aid of the values of K_p, interpolated from Tables II and III

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and given in the second column of Table IV, and the data given in Table I, we may solve Equations 1–5 simultaneously and obtain the partial pressures of the five gases present at equilibrium. Col. 1 gives the absolute temperature, Cols. 3–7 inclusive the partial pressures in atmospheres of the hydrogen, hydrogen sulfide, sulfur dioxide, sulfur and steam, respectively.

TABLE IV.

Temp., abs.	K_{H_2S}.	$[H_2]$.	$[H_2S]$.	$[SO_2]$.	$[S_2]$.	$[H_2O]$.	Log K.
1160	32.8	0.0101	0.111	0.0615	0.117	0.694	5.93
1362	7.98	0.0319	0.090	0.061	0.126	0.685	4.32
1473	4.39	0.0521	0.081	0.067	0.126	0.665	3.59
1473	4.39	0.0566	0.057	0.057	0.053	0.767	3.50
1645	3.20	0.0972	0.044	0.0715	0.051	0.725	2.56

It will be shown in a later paper how these results may be used in the calculation of the free energy of sulfur dioxide. We have given in Col. 8 the log of the equilibrium constant $K_p = [H_2O]^2[H_2S]/[H_2]^3[SO_2]$ for the important reaction $3H_2 + SO_2 = 2H_2O + H_2S$. It is of course possible to calculate from the partial pressures given in Table IV the equilibrium constant for a number of different reactions. These equilibria may best be studied, however, by summing the free energies of the various substances used up and produced in the reactions.

In conclusion the authors wish to thank G. N. Lewis for his kindly interest and many suggestions during the progress of this research.

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[CONTRIBUTION FROM THE PHYSICAL LABORATORY, UNIVERSITY OF MICHIGAN.]

THE SCATTERING OF ALPHA RAYS AS EVIDENCE ON THE PARSON MAGNETON HYPOTHESIS.

BY DAVID L. WEBSTER.

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The essential feature of Parson's theory of atomic structure[1] is the hypothesis that the electron is not a sphere, but a very thin ring, perhaps as much as 1.5×10^{-9} cm. in radius, carrying a charge of negative electricity that circulates around the ring at a very high velocity. This gives it in addition to its electrostatic properties the magnetic properties of a coil of wire carrying a current. This hypothesis was used very successfully by Parson in explaining an extraordinary variety of chemical phenomena, and I have also found it useful as the basis of a theory of heat radiation that is consistent with Planck's law and at the same time with the classical electrodynamical system and the numerous phenomena explained only by that system.[2] The magneton hypothesis, however,

[1] A. L. Parson, "A Magneton Theory of the Structure of the Atom," Smithsonian Miscellaneous Collections, 65, No. 11 (1915).

[2] D. L. Webster, *Proc. Amer. Acad.*, 50, 131–145 (1915).

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has not been generally accepted, one of the chief reasons apparently being that Parson's theory as he developed it calls for a large sphere of diffuse positive electricity, in which the electrons, or magnetons, as he calls them, are free to move. In view of the epoch-making work of Rutherford and Darwin on the large-angle scattering of alpha particles, this positive sphere hypothesis becomes untenable, and the natural impulse in giving it up is to give up the magneton hypothesis with it. In a recent paper in THIS JOURNAL by Langmuir[1] the theory is mentioned as attractive, but dismissed at once because of the positive sphere. If the positive sphere is essential to the magneton theory, this action is necessary. If not, the sooner the two are separated, the better.

But to introduce a nucleus, the assumptions of the theory must be changed, and there is ground for the opinion that the new assumptions are more radical than the old, which are indeed radical enough. In fact G. N. Lewis,[2] in a recent paper in THIS JOURNAL, draws conclusions very much like Parson's from the chemical properties of the elements, but rejects the magneton hypothesis as a working basis, with a reference to a desire to avoid a priori assumptions. The purpose of this paper is therefore, first, to point out the possibility of substituting Rutherford's nucleus for the positive sphere and, second, to make a critical examination of the status of the magneton theory when the nucleus is introduced.

According to Parson, the positive sphere is "little more than a simple mathematical expression for the coherence and rigidity of the atom." With a nucleus exerting no forces but those of electromagnetism, the electrons would all fall into the nucleus. To hold them out, the nucleus must exert some sort of repulsion that is not electrical and varies faster than the inverse square of the distance. For any given distribution of density in the originally assumed positive sphere, it is obvious that there will be a law of variation of this new force that will accomplish the same result, so far as the positions of equilibrium of the magnetons are concerned. In the present state of our knowledge of these positions it is not yet time to attempt to derive from them the necessary law. In any case this non-electrical force, or "mystery force," as some have called it, is a new assumption to add to the theory. The question raised by the evidence of alpha ray scattering is this: Is the evidence for the magneton theory enough to justify all the assumptions involved, now that one more is added? The hypothesis that the electron is magnetic was made to explain an attraction between two electrons at moderate distances that is demanded by chemical phenomena, and the phenomena of radiation demanded also a mystery force of repulsion at short distances between two magnetons very similar to what is now assumed between a magneton

[1] I. Langmuir, THIS JOURNAL, 38, 2221 (1916).

[2] G. N. Lewis, *Ibid.*, 38, 773 (1916).

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and the nucleus. Why, then, do we call the attraction magnetic? Why do we not make that also a mystery force, or as Lewis does, simply assume one law by which repulsion and attraction alternate as one electron approaches another, and make no distinction of different parts of it, one as electric, another as magnetic and a third as neither electric nor magnetic?[1]

There are, as a matter of fact, several reasons for making this distinction. For one, let us consider for a moment the character of the groupings required by chemistry. In general, they are of two sorts, one a pair of electrons closely associated, and the other a very compact group of eight.[2] We never see a group of three, or any other odd number, unless perhaps in the rare compound H_3, which may not even exist at all. Now suppose the law of force between two electrons were that of a repulsion at large distances and very small ones, with an attraction at intermediate ones. Then two electrons brought near each other would stay together in a pair. But a third one would also stick readily to them, or a fourth or a fifth or any number. There would be no tendency to stay in pairs, and certainly no distinction for the number eight. But if the attractive force is that of a pair of doublets, like bar magnets, the pair once formed may be expected to orient themselves oppositely, and thereby cancel each other's attractive forces on a third one approaching from a distance. This means that the grouping in pairs indicates that the attraction is that of doublets, while the repulsions are both spherically symmetrical. The grouping in eights, as Parson has shown, is even stronger evidence in the same direction.

But even granting this, why is the doublet necessarily magnetic, rather than electrostatic? One fact that makes this plausible, but no more, is that magnetization phenomena mean that something in the atom must be magnetic. The assumption that this something is the electron is made highly probable by the data on magnetism collected by Parson, that show paramagnetism wherever chemical phenomena indicate a loose

[1] The mystery force between magnetons might hold them, alone, apart even with a nucleus exerting no mystery force. This suggests the possibility that the nuclear mystery force is unnecessary. But the electromagnetic theorem of no equilibrium in free space makes this impossible, since even if the magnetons were all held in a rigid frame the whole frame would move until one of them struck the nucleus.

Another question that might be asked is why the mechanism holding the electrons away from the nucleus is not centrifugal action in orbits. There are two reasons against this, one the impossibility of stable orbits of the required types, and the other the absolute necessity of a static condition of the atom to explain such phenomena as the stability of shape of asymmetric molecules. The arguments on both of these points are given very clearly, both by Parson (*Loc. cit.*) and in a somewhat different form by Lewis (*Loc. cit.* and especially in *Science*, N. S., **46**, 297 (1917)).

[2] For the arguments on this point, see Parson (*Loc. cit.*) and also Lewis (THIS JOURNAL, **38**, 773 (1916)).

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grouping of some of the electrons. This is exactly what one would expect if the electrons themselves are magnetic.

But even so, why should their magnetism be due to a circulation of the electricity, rather than to magnetic poles? Here the phenomena of diamagnetism are important as evidence of the existence of inductive circuits in the atom; and the obvious instability of the sort of orbital motions that would be required if the electrons were of the classical type[1] indicates that the circulation must be a continuous current. But even this does not prove that the inductive circuits causing diamagnetism are actually the same bodies as the electrons that cause paramagnetism and chemical bonds.

A phenomenon of the greatest importance in this connection is Barnett's effect of magnetization by rotation. In Barnett's experiments[2] it was found that a piece of iron, cobalt or nickel in rotation is magnetized in the absence of any external field. Now if these elementary magnets are electrons moving in orbits, the gyroscopic properties of the orbits would make them behave in exactly this way. Moreover, as Barnett proved, the amount of magnetism to be expected can be predicted from the ratio e/m and the permeability of the metal, all references to the size of the orbit or the speed of rotation having cancelled out in the calculation. The experimental results show quantitative agreement, within limits of error, with the predicted values. Similar agreement was obtained for the inverse effect, rotation by magnetization, in experiments begun later by Einstein and de Haas.[3]

But as we have seen above, and as Barnett says in his latest paper, the assumption of a discrete particle of electricity in an orbit seems untenable, and a continuous current is preferable, provided it will have the proper gyroscopic properties. Now such properties are not a mathematically necessary accompaniment of all forms of translational mass, and the quantitative agreement with the gyroscopic properties of a revolving electron is by no means obvious. The only way to make definite statements on this point is to develop the mathematical theory of the electromagnetic mass and gyroscopic properties of the magneton. This has been done by the present author.[4] It is found to involve not only a treatment of the electromagnetic forces in an accelerated or rotating magneton, but also the internal forces that hold it in shape. On these latter forces we have no very certain data. But making the most plausible assumptions a priori, it is found that formulas for the mass and gyroscopic properties in terms of the charge and dimensions can be obtained, and that these

[1] For further discussion of this point, see Parson (*Loc. cit.*) and Lewis (*Loc. cit.*).

[2] *Science*, **30**, 413 (1909); *Phys. Rev.*, **6**, 239 (1915); *Ibid.*, **10**, 7 (1917).

[3] *Deutsch. Phys. Gesell. Verh.*, **17**, 8, 152 (1915).

[4] *Phys. Rev.*, **9**, 484 (1917).

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formulas make the gyroscopic properties exactly those of a magnetically equivalent orbital electron of the classical type, and therefore exactly those required by the Barnett and Einstein-de Haas effects. This makes it highly probable that the elementary magnets of ferromagnetism, and probably of paramagnetism and chemical bonds also, are really magnetons.

Thus it appears that we can class the magneton hypothesis not as an assumption made a priori, but rather on the surer basis of a most probable deduction from the experimental facts. As such it cannot be lightly tossed aside even if the assumptions that go with it are somewhat complex. Consequently it seems probable that the alpha ray phenomena should not be taken as valid evidence against the magneton theory, but simply as evidence for the existence of the nucleus along with its non-electrical repulsion for magnetons.

ANN ARBOR, MICH.

[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION OF WASHINGTON.]

THERMAL LEAKAGE AND CALORIMETER DESIGN.

BY WALTER P. WHITE.

Received November 15, 1917.

In measuring a quantity of heat in a calorimeter most of the care and time expended is usually demanded, directly or indirectly, on account of the thermal leakage, or interchange of heat between the calorimeter and its environment. Most of the ingenious devices which lend interest to calorimetry have been introduced, wholly or in part, in order to deal with this leakage. And yet until very recently there have been almost no quantitative data upon the effect of the air gap around the calorimeter, although the thickness of this gap, more than anything else, determines the rate of the leakage, and hence the efficiency of any method of dealing with it. As a result it has happened, almost inevitably, that some of the most skilful and carefully planned researches have been conducted with air gaps whose needlessly small dimensions caused an excessive thermal leakage, and so multiplied several times the leakage difficulty or error. One of these researches, for instance, although it incidentally included investigations which led to important improvements in calorimetric method, was yet made with a gap so small (3 mm.) that a change to better dimensions would have brought all the reduction of the leakage and its errors that is obtained by substituting the frail Dewar bulb for a well-designed simple calorimeter. And two very recent articles specially describing improvements in method make mention of air gaps so small (5 and 6 mm.) that they probably neutralized in the apparatus described the advantages gained. On the other hand, in this laboratory a special method dealing with incon-

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stant leakage rates was developed and used, at the cost of considerable labor and inconvenience, for three years, which would have been needless if the air gap around our calorimeters had not been too large.

Within a few months investigations, begun independently at the Bureau of Standards[1] and at the Geophysical Laboratory,[2] have been published bearing on thermal flow in air spaces such as usually surround a calorimeter, which seem to make it now possible to handle thermal leakage with a reasonable approach to maximum effectiveness. The present paper deals with the problem of doing this.

The most important means of reducing the uncertainties due to thermal leakage is undoubtedly a definite control of conditions, such as is secured by proper jacketing, or by preventing evaporation. The last word has not been said regarding such measures, but as far as they are concerned there has been little doubt in which direction efficiency lay, and they are not in view in the present paper, which deals with the effect of the air space around the calorimeter.

It has already been pointed out that a gap of too small dimensions means an insufficient amount of insulating air around the calorimeter. The increase of insulation from an increase in the gap, however, though considerable at first, soon falls off, and before long a minimum point appears beyond which the leakage rate actually increases. But even before this point is reached another difficulty is encountered; the leakage ceases to be sufficiently nearly proportional to the *thermal head*, or temperature difference between the emitting and the receiving surface. That is, Newton's Law of Cooling, on which nearly all methods of treating the leakage are based, fails to hold. The advantage of the law is merely its simplicity; a different law can be made to give satisfactory accuracy even over 20° intervals.[3] But there is little doubt that most experimenters would very greatly prefer to retain the simpler methods; moreover, the point of minimum leakage ordinarily is not so very far beyond the point where the variation from Newton's Law becomes troublesome, so that the experimenter will gain but little who disregards the variation from the law in endeavoring to get the absolute minimum of leakage. It therefore seems best in this paper to take a following of Newton's Law as one of the requirements which is to be met in deciding upon the size of air gap.

Transfer of heat through the air may occur by radiation, conduction, convection, and evaporation, and in connection with these it seems best

[1] "The Testing of Thermal Insulators," H. C. Dickinson and M. S. Van Dusen, *A. S. R. E. Journal*, 3, 5 (1916).

[2] "Heat Convection in Air, and Newton's Law of Cooling," Walter P. White, *Phys. Rev.*, 10, 743 (1917).

[3] See, *e. g.*, "Some Calorimetric Methods," Walter P. White, *Phys. Rev.*, 31, 553–557 (1910).

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to consider the heat capacity of the air. Of these various things we may say at once, with sufficient accuracy for all practical purposes:

1. The heat capacity depends on the amount of air alone.

2. Radiation depends on the area of the calorimeter surface, and on the character of that and the surrounding surfaces.

3. Conduction depends in a known way on the dimensions of the air layer.

4. Evaporation presents two aspects: there may be, first, a change in the saturation of the air space, which is avoided only by preventing evaporation altogether, and second, distillation, which is avoided in the strictly adiabatic method, and also (T. W. Richards) by keeping the calorimeter always colder than the environment.

Of all these factors, evaporation is the most uncertain. It may vary with the actual temperature, with the temperature difference of calorimeter and environment, and with the geometry of the air space, and is very sensitive to the presence of films on the surface of the liquid. Its effects are liable to considerable lag. It causes the cooling to follow an altogether different law if the thermal head (temperature difference) changes sign.[1] The safest and also the simplest way to proceed is of course to prevent evaporation, unless doing so brings greater disadvantages.

The other factors show practically no lag, and no uncertainties not chargeable to imperfect knowledge of the temperatures concerned.[2] They do show, however, a variation from Newton's Law, that is, a lack of strict proportionality between leakage and thermal head, which next demands examination.

It follows readily from familiar laws, and with far greater accuracy of approximation than is needed in practical calorimetry, that for a given mean temperature radiation and conduction are simply proportional to the thermal head, but that with increasing mean temperature of the two surfaces concerned radiation increases about 1% per degree at room temperatures, and conduction 0.0017 per degree. It therefore follows that: (1) if the mean temperature changes from day to day or from season to season the thermal leakage will bear a different ratio to the thermal head, that is, to the interval; but this will ordinarily not interfere with the cus-

[1] "The Adiabatic Determination of the Heats of Solution of Metals in Acids," T. W. Richards and L. L. Burgess (THIS JOURNAL, 32, 449 (1910)).

Measurements made in our laboratory by Mr. E. R. Edson, of the Mellon Institute, show that for a free water surface 1 cm. below the top of the calorimeter chamber the excess heat transfer with jacket colder will be about 0.01 calorie per minute per square cm. for 1° of thermal head, corresponding to a variation of about three-tenths in the thermal leakage of an ordinary calorimeter holding about a liter, with 1 cm. gap. It involves 1 mg. per *hour* per sq. cm. per degree.

[2] Radiation will, of course, vary with the cleanness or chemical condition of the surfaces. But it is not likely to change from these causes *during a determination*.

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tomary calculation of the "cooling correction" by assuming Newton's Law;[1] (2) for constant environment (*i. e.*, constant jacket temperature) during an experiment, where any given change in the calorimeter evidently produces half as much change in the mean temperature of both, the heat leakage from conduction and radiation will not be proportional to the interval and the variation from proportionality will be for a given change in the interval half as great as that stated above for a variation in the mean temperature.

This variation from Newton's Law is clearly inevitable, but it is fortunately very small. For both these reasons it may here be dismissed without further consideration.

With regard to convection the situation is very different. In convection we have the motion of bodies of air whose temperature differences are proportional to the differences between the solid surfaces. But the velocities of these air currents will evidently also increase with this temperature difference. Hence the heat transferred will increase more than in proportion to the temperature difference. During every calorimetric determination where the temperature difference of calorimeter and environ-

TABLE I.

Heat transfer, in the usual cgs unit, *i. e.*, calories per second per degree of thermal head per sq. cm. of flat surface, at 22.8° *mean* temperature.

Where two values are given they show the range among determinations with different methods of getting the temperature of the outer plate. It will be seen that the value of the convection is practically unaffected by this difference of method.

Thermal head.	8 mm. gap.		12 mm. gap.		24 mm. gap.	
	Total.	Convection.	Total.	Convection.	Total.	Convection.
0.99°	....	....	0.0000839	.....	0.000065	....
			0.0000848	.....	....	....
1.98°	0.000109	....	0.0000840	0.0000001	....	....
	110	....	0.0000852	0004	....	....
4.95°	0.000111	0.000001	0.0000866	0.0000028	0.000090	over
	....	....	881	0037	....	0.000025
9.89°	0.000112	0.000003	0.0000937	0.000010	0.000106	over
	113	003	952	0.000011	....	0.000040
19.76°	0.000116	0.000007	0.0001077	0.000024	0.000126	over
	....	....	1094	026	....	0.000060

ment varies appreciably (as it usually does) the convection transfer will vary by a large part of itself, and Newton's Law will hold for the whole transfer only if the convection is relatively small. The problem of securing a constant ratio of thermal leakage to temperature difference in calorimetry

[1] This variation, however, should have been taken account of in a previous paper of mine, where I discussed the possibility of computing the cooling correction from a known value of the heat leakage ratio. ("Lag Effects and Other Errors in Calorimetry," *Phys. Rev.*, 31, 577 (1910).)

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is then, practically, the problem of diminishing convection. The difficulty of this problem lies in this: convection increases with the thickness of the air layer between calorimeter and jacket, and is thus made larger by the very same procedure which diminishes the conduction and therefore tends to diminish the total thermal leakage. The designer of a calorimeter must therefore strike a balance between opposing advantages, and will want to know how thin to make the air layer in order to just avoid undesirable convection without unnecessarily increasing conduction.

Table I and Fig. 1, taken from the paper on convection in air already referred to, show the actual values of convection for the calorimetric range and for spaces 8 cm. high. These values are probably a little high, perhaps 10%, but this uncertainty is less than others present in convection phenomena, and does not impair the practical value of the results. These results, for narrow gaps, follow fairly well the laws, obtained theoretically: (1) The total convection heat transfer is independent of height, that is, the transfer per sq. cm. is inversely proportional to height. Convection heat transfer is proportional (2) to the square of the temperature difference, and (3) to the cube of the gap width. As the temperature difference increases there is a tendency for the transfer to increase more rapidly than according to (2), which appears clearly in the 12 mm. gap results; with still more vigorous convection the increase with temperature grows less, as appears with the 12 mm. gap for 20° thermal head, and very markedly with 24 mm. These variations from the simple laws are probably due to the develop-

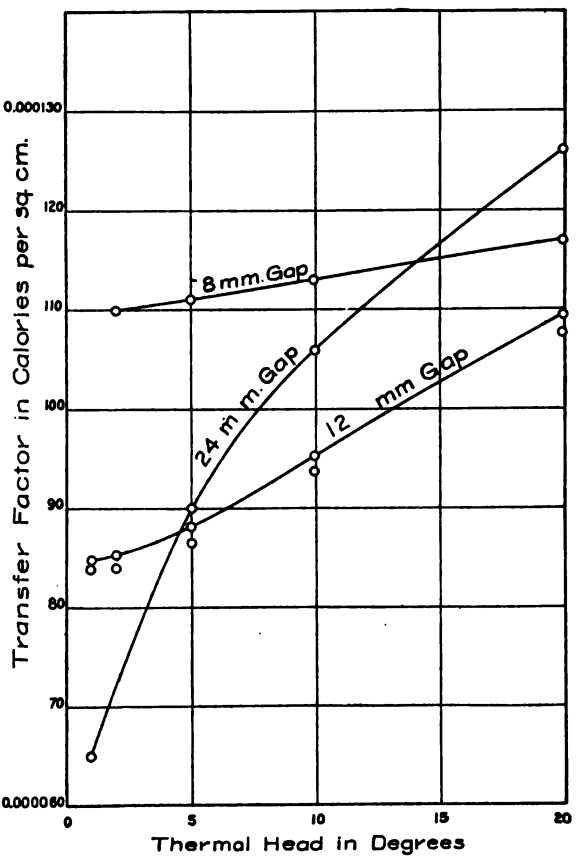

Fig. 1.—Rate of heat transfer through the air for different widths of air gap between plates 8 cm. high.

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ment of turbulence. The quantity actually shown in Fig. 1 and Table I is not the the total heat transfer, but is the heat transfer factor, or transfer per unit of thermal head (temperature difference) which is constant when Newton's Law holds.

1. Width of the Air Gap around the Calorimeter.

For the present purpose, the most significant thing about convection is that it varies about as the cube of the gap width. From this fact it follows that large changes in convection can be made at the cost of slight ones in conduction. Hence comes the practical rule; make the width small enough to render convection negligible and stop there; to go any further will only increase conduction; to go in the opposite direction will increase convection rapidly while giving only a slight gain in decreasing conduction. What is necessary to make convection practically negligible depends on the required precision, the time, and the temperature range, and can be estimated for given conditions. Such an estimate can be made as follows: In the first place it has been shown[1] that in the most unfavorable case an unregarded deviation from Newton's Law produces an error in the thermal leakage allowance (cooling correction) about equal to one-sixth of an allowance calculated by taking the deviation alone as the cooling rate—that is, about equal to $^1/_6 Tk' \Delta\theta$, where T is the time, $\Delta\theta$ the change in calorimeter temperature, and k' the change in the leakage factor due to the change $\Delta\theta$. In nearly all cases likely to occur in practice the error is much less than half that given by this rule, so that by taking $^1/_6$ as the numerical coefficient we are allowing a large factor of safety. If, now, we suppose that the high precision of 0.1 per mille is sought, that is, a precision of 0.0001 $\Delta\theta$, the maximum allowable variation from Newton's Law will be such as to make $^1/_6 Tk' \Delta\theta$ equal to 0.0001 $\Delta\theta$ and this, for a 10-minute interval, gives k' as 0.000001 per second. If we suppose, further, that the calorimeter holds a liter, its surface will be around 600 sq. cm. or 0.6 sq. cm. for each gram of water, so that the allowable variation of 0.000001 per second will be 0.000001 per 0.6 sq. cm., or 0.0000017 per sq. cm. per second. This means that the change in the thermal head may be allowed to change the convection rate by 0.0000017 cal. per degree per sq. cm. per second. (This would ordinarily be from 2.5 to 3% of the total thermal leakage, but has the same absolute value whatever the total leakage may be.) A glance at Table I shows that the convection factor 0.0000017 would be reached in a 12 mm. gap at a temperature interval of about 3°, for a 1 cm. gap at about 5°, while an 8 mm. gap would make a 7° interval permissible. If the calorimeter should hold nearer 2 liters it would probably be 16 cm. high; in that case the convection effect would be half of that recorded in Table I for 8 cm. plates, and the safe temperature limits would be around 5° for 12 mm. gap thickness,

[1] "Some Calorimetric Methods," *Loc. cit.*; p. 554.

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7° for 1 cm. and 10° for 8 mm. If the precision desired should be 0.3 per mille, a precision which has proved sufficient for researches of great value, the convection factor may be 0.000005 per sq. cm. per second, and the safe gap for a 5° interval (and 16 cm. height) is 17 mm. This is not so very different from 12 mm., the value for three times as great precision, but it seems well worth while to know that it, rather than 8 mm., or even 1 cm., is the permissible limit, since a doubling of the narrow gap cuts in two (approximately) not only the total thermal leakage, but most lag effects,[1] and errors from uncertain temperature distributions.

It is impossible to say much as to the permissible gap width for differences of 1° or less, since it is evident that the precision of the measurements, high as it was, was not sufficient for the exceedingly small quantities involved. The course of the 24 mm. curve in Fig. 1 shows that convection was appreciable at 1° for that gap width. But for differences of a few tenths of a degree it seems safe to apply the general laws stated above; these lead to the conclusion that gaps as great as 3 cm. may sometimes be advantageous in such cases.

If the time of the experiment is longer, the thermal leakage allowance will be greater (other things equal, of course), and less convection can be tolerated. Herein lies an additional reason for favoring the adiabatic method in protracted determinations.

2. Large vs. Small Calorimeters.

The choice of the best dimensions is of course presented to nearly every designer of calorimeters, and has received much more attention than the more important question of the air gap. All previous discussions of size (including my own) treat the rate of thermal leakage as proportional only to surface and thermal head, which evidently involves the assumption that the thickness of the air gap must or should be the same regardless of the size of the calorimeter. Of course the conclusions reached will be modified as soon as we take account of the fact that the gap can advantageously be larger for a larger calorimeter. The modification, to be sure, is not at all striking, but it involves a quantity about as large as the original result, and so seems worth noticing. Another reason for taking up the matter is that all conclusions so far stated are unsatisfactory, even on the basis of an unvaried air gap thickness. The almost universal conclusion hitherto has been that since in the larger calorimeter the ratio of surface to mass is less, and the calorimeter consequently leaks less of the heat imparted to it, it is bound to give less thermal leakage error.[2] Making a

[1] This follows directly from the lag equation given further on.

[2] The argument, here and elsewhere, applies to calorimeters measuring the same quantity of heat; if the heat can be made proportional to the size of the calorimeter, as often in thermochemical work, there is no question that the larger vessel and larger heat quantity give a more accurate measurement in a stirred calorimeter. *In aneroid*

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logical application of this reasoning, A. Magnus even[1] used vessels holding 60 liters. This conclusion I have ventured to condemn,[2] taking the ground that the principal source of error lies usually not in the temperature change within the calorimeter but in the uncertainty of the environing (jacket) temperature. There is of course no question that in the larger calorimeter with larger surface a given external temperature difference will cause a greater total flow of heat, and an external discrepancy will therefore cause a greater error. My underlying assumption, however, has been challenged by a high authority, who holds that the main source of error is not without, but within, the calorimeter. It therefore seems worth while to show further that error from internal causes tends to be less in a small calorimeter, provided we treat the gap thickness as fixed. It does not seem legitimate to assume that the leakage error is necessarily larger where the leakage itself is larger. The causes of error need to be examined. (1) It is clear in the first place that the mere measurement of the calorimeter temperature need never cause appreciable error in determining the thermal leakage, since this leakage is a small fraction of the total heat measured, and we can, if necessary, use the same thermometric precision for one as for the other. There remain, as sources of error, (2) the lack of uniformity of the calorimeter temperature and (3) lag effects.[3] Most lag effects are greater with a small calorimeter (see Equation 1, below) but most of them (including the thermometer lag) are constant, and therefore introduce no error in a calibrated calorimeter. The only exception is the lag of the internal temperature, but this lag depends entirely upon the lack of uniformity of temperature, already given as one source of error. And since this uniformity depends upon stirring, the question at issue resolves itself into this: "Is it easier to stir effectively a large or a sma calorimeter?" If n is the ratio of the linear dimensions of the two calorimeters then the ratio of their surfaces will be n^2, of their volumes, n^3. I we make the very probable assumption that temperature equalization is proportional to the quickness with which the water makes a circuit, that is, to the speed with which it moves divided by the length of its path, then since in the larger calorimeter the temperature differences will originally tend to average $1/n^3$ times as great, on account of the greater mass to be heated, the differences left by the stirring will be $1/n^3 \div V/n$ times as great, and hence the

calorimeters, however, this is far from true; an important point which may be considered further at another time.

[1] "Ueber die Bestimmung spezifischen Wärmen," A. Magnus, *Ann. Physik.*, 31, 598 (1910).

[2] "Easy Calorimetric Methods of High Precision," Walter P. White, THIS JOURNAL, 36, 2317 (1914).

[3] In adiabatic work a timing error on the observer's part may enter. Hence the conclusions of this section do not apply strictly to adiabatic methods, which are considered in the next section.

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resulting chance of error from insufficient stirring, equal to these differences multiplied by the n^2 times as great chance of loss of heat from the greater surface, will be $1/V$ times as great, that is, independent of the size, but inversely proportional to the speed. But the heat of stirring is probably approximately proportional to ldV^3, where l and d are length and diameter of the path of stirring,[1] that is, to n^2V^3. Hence for constant heat of stirring, n^2V^3 constant, the error due to imperfect equalization, being proportional to $1/V$, is proportional to $\sqrt[3]{n^2}$, a result which reinforces slightly that obtained by considering the external uncertainties, and is opposite to and about as large as the result generally reached; that is, it makes the smaller calorimeter nominally less liable to error.

The experimenter who tries to suit his air gap to the other conditions of his work will find this conclusion modified as follows: As far as the *conduction* through the air is concerned, or the heat capacity of the surrounding air, it is fairly evident that any principles which may govern the gap width for any calorimeter will call for a gap thickness approximately proportional to the linear dimension, that is, to n. As to convection, we have the temperature interval only $1/n^3$ for the larger calorimeter; the circumference, n times as great, will tend to increase convection n times; the change in height produces no effect; the convection from the ends increases as n^2. The change in *calorimeter* dimensions thus decreases the convection a little less than n^2 times, which may be offset by increasing the gap nearly $\sqrt[3]{n^2}$ times, since convection varies as the cube of the gap thickness. The final result is to make the effect of a change in dimensions even less important than it is for unvaried gap thickness, as far as internal sources of error are concerned. The effect of external irregularity remains considerable, though diminished.

The practical conclusion seems to be that the size of the calorimeter is, within limits, of very little importance as far as thermal leakage is concerned provided it is not forgotten that the jacket temperature needs to be kept uniform with more and more care as the calorimeter becomes larger. There will rarely be a question of changing the capacity by more than a factor of 10, so that n will seldom much exceed 2, in any case.

3. Adiabatic Calorimetry.

One exception should probably be made to the statement that the size of the calorimeter is ordinarily unimportant as regards thermal leakage, and that is in adiabatic work. It has been sometimes recognized, though apparently not yet definitely stated in the literature, that usually in adiabatic work no convection and therefore no deviation from Newton's Law is to be feared, and hence that that method has a peculiar advantage where

[1] This rule is derived by multiplying the ordinary engineer's formula for the friction head by Vd. This gives $VPd^2 \propto ldV^3$ (P = pressure), and the first member is evidently the rate of doing work on the circulating stream, and therefore equivalent to the heat.

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large temperature differences are necessary or desirable, that is, with small calorimeters. The method, however, is easier to operate with large calorimeters, for the following reason: The conduct of an adiabatic determination calls for more or less rapid adjusting of the jacket temperature to the varying temperature in the calorimeter, and the effect of a delay in this adjustment is similar to a lag. The general formula for a lag[1] effect or error is

$$LK\Delta\theta, \qquad (1)$$

where L is the lag in minutes or other unit of time, K is the thermal leakage factor of the calorimeter in the same unit, and $\Delta\theta$ is the temperature rise. It follows from this formula that the time error in the adiabatic adjustment diminishes as the thermal leakage factor. The large calorimeter thus has an advantage in any case, but the advantage may be augmented by increasing the air gap, as recommended above. If such an increase makes it possible to get the same quasi-lag effect by following the calorimeter temperature within 10 seconds instead of 5, the advantage may be almost a doubling of the precision of the thermal leakage elimination.

This kind of gain may be carried still further in adiabatic work. If there is nothing to fear from convection, the gap, in calorimeters both small and large, may be made considerably larger than in ordinary, non-adiabatic (merodiabatic?) methods, diminishing the thermal leakage factor, and with it, all lag errors as well as the heat produced in stirring. This possibility adds new value to the adiabatic method in general.

There is perhaps less real difference of opinion now existing as to the adiabatic method than might appear from the literature, some of which is not so very recent, but this is, if anything, rather a reason why attempts at restatement regarding the method might be worth while. When it was first employed and advocated by T. W. Richards, in 1905, the sources of calorimetric error had received very little systematic study, and, more particularly, the various lags had not even been listed, and were mainly known as indefinite possibilities of error. This entanglement of uncertainties was outflanked by the adiabatic method, which seemed to reduce the whole problem to simpler terms. Since that time, direct attacks on the problem have changed the situation materially. The lags have proved to be decidedly different from what was at first surmised,[2] and it has been shown[3] that the redoubtable error in the thermal leakage determination becomes absolutely negligible (ordinarily) if there is applied to it the same means which are necessary with the adiabatic method, namely, a complete

[1] W. Jaeger and H. von Steinwehr, *Verh. der Deutsch. Physik. Ges.*, **5**, 50, 353 (1903); *Z. Physik. Chem.*, **54**, 428 (1906); W. P. White, *Phys. Rev.*, **31**, 569 (1910).

[2] "Lag Effects and Other Errors in Calorimetry," Walter P. White, *Phys. Rev.*, **31**, 562 (1910).

[3] "A Test of Calorimetric Accuracy," Walter P. White, *Phys. Rev.*, **31**, 696 (1910).

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inclosing jacket, whose temperature is measured. Dickinson,[1] also, emphasized still further the fact that the adiabatic is liable to much the same errors as the ordinary method. In fact, the conclusion was reached that for ordinary calorimetric experiments, lasting ten minutes or less, the adiabatic method does not so much avoid or destroy the thermal leakage errors as furnish a valuable alternative method of dealing with them, although for protracted determinations or aneroid calorimeters it is usually superior. The consequences of this conclusion are exemplified in the practice of the Bureau of Standards. The adiabatic method is used exclusively in aneroid calorimetry, where it is indispensable, but for ordinary calorimeters it is used alongside the older method as a means of diminishing *systematic* errors, and with results neither better no worse than those given by the older method.

But while it is clear, as a result of increased knowledge and of the improvement of ordinary methods, that the adiabatic can no longer claim, in ordinary work, the unique superiority which it originally had, it has, nevertheless, several recognizable advantages which do not appear to have been stated.

Two of these are those already mentioned, which arise out of the disappearance of convection in the adiabatic method: First, the greater *ease* with which large temperature rises can be handled, and second, the greater *precision* which should result when the thermal leakage factor is diminished by increasing the air gap.

The use of wide gaps in this way, however, is subject to three restrictions.

1. Of course it will not do unless the calorimeter is to be confined to adiabatic work.

2. The large air space increases evaporation trouble, and its use will generally make it desirable or necessary to seal the calorimeter altogether against evaporation. That is to say, the experimenter by virtue of the adiabatic method may have *either* freedom from distillation *or* a specially small thermal leakage factor, but can not, in general, have both.

3. The wide gap must be applied with caution to rapid temperature changes. For instance, if an experimenter, thinking that convection was banished, should reduce the thermal leakage factor of a small calorimeter to 0.001 by using a gap of 4 cm. and should therefore suppose that he might permit a lag of 20 seconds in his jacket temperature, and act on that supposition in a determination where a rise of 3° occurred in the first minute he would have a thermal head of 1°, and convection enough to make his calculations false by perhaps 100%.

Another unstated advantage of the adiabatic method is its effect in

[1] "Combustion Calorimetry and the Heats of Combustion of Cane Sugar, Benzoic Acid, and Naphthalene," H. C. Dickinson, *Bull. Bur. Standards*, 11, 206 (1914).

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diminishing evaporation errors by (practically) avoiding distillation,[1] leaving only the slight increase in the saturation of the air gap which comes with changes of temperature. Dickinson and I, in our earlier discussions of the adiabatic method, both had in mind, and I expressly specified,[2] calorimeters such as we were using, in which evaporation was prevented altogether. There is little doubt that this is in general the most accurate practice. Nevertheless, where circumstances still counsel the use of open calorimeters the adiabatic method evidently has a distinct advantage. T. W. Richards and his school have often availed themselves of it.[3]

Professor Richards has called my attention to a possible calorimetric error which indirectly has some bearing on the adiabatic method, though it is itself a question of lag. In a discussion of thermometric lag[4] which was repeated in neater mathematical form, by Harper,[5] I stated that in calorimetry the lag was negligible *if the same thermometer was used* in the calorimeter *for both final and transfer period readings*. The reason for this, as shown in the discussion, is that the lag of the thermometer during the main temperature rise of the calorimeter will then exactly offset the lag effect which occurs while the calorimeter is cooling. Professor Richards points out, however, that in determinations of heat of mixing there has frequently been no attempt to follow the almost instantaneous temperature rise with the thermometer; the rise has been dated from the time of mixing; the final temperature reading therefore has its lag error uncompensated by the usual earlier reading; and yet the rule has been complied with of using but one thermometer. The difficulty, of course, is merely a matter of statement or interpretation of the rule; to date the temperature rise from the actual mixing is *equivalent* to measuring it with a lagless thermometer, that is, a different one from that used to read the final temperature. Properly understood, the rule covers the case perfectly; its spirit is violated by the procedure pointed out by Professor Richards; a restatement, more explicitly covering this case, removes all difficulty, and is of course desirable. If we say: "There is no error from thermometer lag *if the thermal behavior of the calorimeter is determined throughout by the*

[1] Dr. Dickinson suggests that the adiabatic method is still subject to this limitation; it cannot avoid distillation from an open calorimeter if used in the valuable form (H. C. Dickinson, *Loc. cit.*, p. 207) where the *mean* thermal head, and not the instantaneous head, is kept equal to zero.

[2] "Lag Effects and Other Errors in Calorimetry," *Loc. cit.*, p. 576.

[3] The discussion immediately preceding has dealt mainly with the question of *precision*. Of course the adiabatic method may under various circumstances have advantages in *convenience* where both it and the ordinary method are more than sufficient in precision, as they usually are.

[4] "Lag Effects," *Loc. cit.*, p. 565.

[5] "Thermometric Lag," R. N. Harper, 2nd, *Bull. Bur. Stand.*, 8, 706 (1912).

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same thermometer,"[1] all chance of mistake seems removed. This matter affords a good illustration of the logical simplification introduced by the adiabatic method, for with that method in universal use the problem would never have arisen. Of course it is also possible to get correct results by thermal observations on the temperature rise, or by making a correction for the lag.

4. "Radiation" Shields.

Shields of thin metal between calorimeter and jacket are still described and used. If we suppose that the total air gap is not altered on their account, it is fairly evident that conduction through the air is scarcely affected, though radiation, usually a subordinate cause of thermal leakage, is diminished to one-half for a single shield. Convection is greatly diminished, but this is not important if Newton's Law is holding in the first place, as it usually is. If, however, we suppose that in the shielded calorimeter each gap is as great as the single gap without a shield, it is clear that heat transfer both by conduction and by convection is also reduced nearly to half value in the shielded arrangement, whose main advantage is that it enables conduction to be diminished without increasing convection. It is doubtful if this has been generally recognized. The shield is preferably called a *convection shield*.

Another thing not always recognized regarding such a shield is that it adds something to the *effective* heat capacity of the calorimeter. There are cases where an experimenter has determined the heat capacity of his calorimeter by calculation, without taking any account of the shield. The capacity effect (on the calorimeter) of the shield is very different from the capacity of the shield, and is, in general, hard to determine exactly. But a demonstration which I hope soon to publish shows that, whatever may be the form of the curve expressing the temperature change in the calorimeter, the net final effect of the heat capacity of the shield is always the same (for constant jacket temperature), and proportional to the temperature interval, so that it is a typical lag (Equation 1), in being equivalent to a small *constant* term added to the calorimeter heat capacity.[2] This term depends on the rate of transfer of heat to and from the shield, and therefore varies (on account of the change in radiation) if the condition of any of the surfaces concerned changes, and also, of course, if the shield is displaced. It is of course important that this fact should not be forgotten, but with constancy of conditions preserved the shield would introduce no error in a *calibrated* calorimeter. If the shield is midway between calorimeter and jacket surface, its effective heat capacity is about $^1/_4$ its true capacity. The change in this constant capacity from a shift in the

[1] That is, if a complete temperature curve for every part of the experiment is obtained.

[2] It is not proportional to K, however, and in this it differs from other lags.

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position, or a one-sided change in the radiating power, of any portion of the shield is proportional to the change in distance from the calorimeter, or, to the total change in emissivity. It follows that the shield should be as thin as is mechanically possible; it should never be thicker than 0.1 mm. At 0.1 mm. its effective capacity will seldom exceed, though it may approach, 1 per mille of the total calorimeter capacity.[1]

With two shields the leakage factor of a very well designed calorimeter can be reduced to about 0.4 of its original value. This gain is almost as great as can be secured by using a vacuum-jacketed vessel, and is obtained in a way which is vastly preferable in many cases.

It is also possible, by using a thin shield and running thermoelements from it to the jacket wall, to determine or eliminate the thermal leakage more accurately than by the customary arrangements, and even more accurately and more conveniently than by putting thermoelements directly on the calorimeter. The full discussion of this improvement, however, seems to belong in another connection.

5. Heat Capacity of the Air.

The demonstration just mentioned shows that the net final effect of the heat capacity of the air around the calorimeter is also equivalent to a nearly constant addition to the heat capacity of the calorimeter. This result is important to the purposes of the present paper, since it shows that there is no heat capacity error introduced in a calibrated calorimeter by using the wide air gaps here recommended for certain cases.

The effective capacity of the air will rarely reach 0.001 that of the full calorimeter, and even then a temperature change of 20° or a barometer change of 5 cm. will be required in order to change this extreme value by 0.00007 of the total heat capacity.

Summary.

The interchange of heat between a calorimeter and its environment (thermal leakage) is practically proportional to their temperature difference except for the effect of evaporation, and for that of convection, which is, for ordinary calorimetric conditions, more nearly proportional to the square of that difference.

1. If evaporation is suppressed the advantages of a constant thermal leakage factor are obtained by preventing convection. Recent investigations upon convection show how this may most advantageously be done. Diminishing the width of the air gap around the calorimeter diminishes convection very rapidly, and this can be carried far enough to be effectual without too great an increase of the total thermal leakage, which is then

[1] Dickinson ("Combustion Calorimetry," etc., *Loc. cit.*, p. 201) has also discussed the "radiation" shield though with results very different indeed from those indicated here. Further discussion of the differences will come more properly with the proof of my own statements.

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mainly due to *conduction*, and therefore increases about in inverse proportion to the gap width. Gaps of from 1 cm. to 1.7 cm. according to circumstances, are best with ordinary calorimeters.

2. With large calorimeters, where the temperature change is less, freedom from detrimental convection is compatible with gap widths greater than those most desirable for small calorimeters.

3. In adiabatic work there is little fear of convection, hence either very large temperature intervals or very large air gaps can be profitably employed.

4. Very thin reflecting shields around the calorimeter may be used so as to diminish conduction, and thus decrease the total thermal leakage, without increasing convection.

5. Incidentally, it is pointed out that the ordinary rule, that thermometer lag causes no error where only one thermometer is used, deserves careful interpretation, or else re-statement, in the case of some thermochemical determinations.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

THE FREE ENERGY OF DILUTION OF SULFURIC ACID.

BY MERLE RANDALL AND O. E. CUSHMAN.

Received November 16, 1917.

The number of accurate measurements from which the free energy of dilution of electrolytes involving bivalent ions may be calculated is limited. We have, at present, insufficient data, except in very dilute solutions, from which to calculate the degree of ionization or the activity of the ions of substances such as sulfuric acid. The occurrence of intermediate ions, such as HSO_4^-, which are probably present in considerable amount, and our inability to estimate their concentration, makes the problem of the interpretation of the result even less certain.

Lewis and Lacey[1] have studied the e. m. f. of the cell

$$H_2,\ H_2SO_4(aq),\ Hg_2SO_4,\ Hg,$$

at the two concentrations of sulfuric acid, 0.005 and 0.05 *M*. They found

$$H_2,\ H_2SO_4\ 0.05\ M,\ Hg_2SO_4,\ Hg;\ \mathbf{E}_{298} = 0.7545.$$

$$H_2,\ H_2SO_4\ 0.005\ M,\ Hg_2SO_4,\ Hg;\ \mathbf{E}_{298} = 0.8160.$$

Cells of this type have no liquid potential and the electromotive force determines the free energy of the reaction.[2]

Brönsted[3] has studied the above cell at various temperatures and over

[1] Lewis and Lacey, THIS JOURNAL, 36, 804 (1914).

[2] $\Delta F = -n\mathbf{E}F$. Lewis, *Ibid.*, 35, 1 (1913).

[3] Brönsted, *Z. physik. Chem.*, 68, 693 (1910).

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a rather wide range of concentrations. His results will be discussed in a later section.

In this investigation the e. m. f. at 25° between hydrogen and mercurous sulfate electrodes in sulfuric acid at mol fractions 0.0009102 to 0.1288 has been determined.

Hydrogen and Mercurous Sulfate Electrodes.—The hydrogen electrodes were the same type as those described by Lewis and Rupert,[1] and by Lewis, Sebastian and Brighton.[2] The platinum electrode was covered with a thin layer of iridium black produced by depositing from a five per cent. solution of iridium sesquichloride. A very low current density was used and the direction of the current reversed for a few seconds every two minutes.

The hydrogen was produced in the electrolytic generator used by Lewis, Sebastian and Brighton. The sulfuric acid was prepared by diluting C. P. acid with conductivity water. The solutions at mol fraction 0.0009102 and 0.009014 were compared with 0.1 *M* and 1 *M* hydrochloric acid which was in turn standardized against silver chloride. Sulfuric acid of mol fraction 0.01824–0.1288 was standardized against fused sodium carbonate.[3]

The mercurous sulfate electrodes were of the usual form. They were prepared from pure mercury and from mercurous sulfate obtained by the method of Hulett.[4] These substances were shaken with the sulfuric acid, the solution decanted, and the process repeated several times as in the usual preparation of calomel electrodes. These electrodes were very constant in all the solutions used, and were reproducible to 0.0001 volt. If sulfuric acid is allowed to come in contact with the platinum lead wire the electrode is not constant or reproducible. The cell is therefore thoroughly dried, about 0.5 cc. of dry mercury added, and then the mixture of mercury, mercurous sulfate and sulfuric acid. Care is taken in stirring not to disturb the mercury at the botton of the cell.

Three mercurous electrodes (Cells 1, 2 and 3) and the hydrogen electrode were dipped into a single intermediate vessel. The measurements are given in Table I. The first column gives the mol fraction of the sulfuric acid, the second, third and fourth columns give the e. m. f. measured against different sulfate electrodes, the fifth the barometric pressure, the sixth the mean value of each hydrogen electrode corrected for hydrogen at one atmosphere,[5] and the seventh the final mean. Each row represents

[1] Lewis and Rupert, THIS JOURNAL, 33, 299 (1911).

[2] Lewis, Sebastian and Brighton, *Ibid.*, 39, 2245 (1917).

[3] The carbonate method is the more accurate, and was used in those measurements made after the experiments with this method. Richards and Hoover, THIS JOURNAL, 37, 95, 108 (1915); Randall and Scafione, *Met. Chem. Eng.*, 13, 787 (1915).

[4] Hulett, *Phys. Rev.*, 32, 257 (1911).

[5] Lewis, THIS JOURNAL, 35, 1 (1913).

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a new filling of the hydrogen electrode. The values for 0.005 *M* and 0.05 *M* acid obtained by Lewis and Lacey are given in the first two rows of the table.

TABLE I.

E. M. F. of the Cell H_2, H_2SO_4, Hg_2SO_4, Hg.

Mol fraction. *N.*	E cell. 1.	E cell 2.	E cell. 3.	Press. Cm.	$E_{corr.}$	$E_{mean.}$
0.00009009	..	..	..	..	..	0.8160
0.0008999	..	..	..	..	..	0.7545
0.0009102	0.7538	0.7540	..	75.7	0.7544	..
....	..	0.7541	0.7540	75.3	0.7545	..
....	..	0.7540	0.7539	75.8	0.7543	0.7544
0.009014	0.6956	0.6956	..	76.0	0.6960	..
....	0.6954	0.6954	..	75.3	0.6959	..
....	0.6953	0.6953	..	74.7	0.6960	..
....	0.6954	0.6954	0.6954	74.9	0.6960	..
....	0.6954	0.6954	..	75.3	0.6960	0.6960
0.01824	0.6745	0.6746	0.6746	75.5	0.6751	..
....	0.6744	0.6744	0.6744	74.8	0.6751	..
....	..	0.6743	0.6742	74.8	0.6750	0.6751
0.06149	0.6183	0.6182	0.6182	75.9	0.6187	..
....	0.6181	0.6183	0.6184	75.5	0.6186	0.6187
0.1288	0.5503	0.5502	0.5501	75.6	0.5506	0.5506

The values of the e. m. f. given in the table are the values obtained after the hydrogen had bubbled through the cell for several days and the value had become steady. In the case of the three most concentrated acids, the hydrogen, after leaving the cell, was bubbled through a small washing tube[1] containing a few cc. of 0.01 *M* I_2 solution. In no case was there an appreciable change in the iodine concentration due to formation of SO_2. We may thus assume that the rate of reduction of sulfuric acid by hydrogen is too slow to affect our measurements. The free energy of the reaction

$$H_2 + Hg_2SO_4 = H_2SO_4(\text{aq. } N = x) + 2Hg, \qquad (1)$$

is given in the last column.

Edgar[2] has also measured this cell at several concentrations. His measurements were made at 25° in an apparatus similar to that used by the writers. The results are given in Table II and are marked E. Brönsted's[3]

[1] Cumming, *Trans. Faraday Soc.*, 6, 10 (1910).

[2] See Lewis, Randall and Bichowsky, THIS JOURNAL, 40, 356 (1918).

[3] Brönsted, *Z. physik. Chem.*, 68, 693 (1910). From a study of Tables 18, 19 and 20 of Brönsted's paper it is evident that the values of π given in Table 18 for $x = 0.02175$ are for a concentration $x = 0.04255$. In order to obtain a value for 25° at $x = 0.02175$ the values of Table 20 were reduced to 1 atmos. H_2 at the temperatures given and the value interpolated for 25°. The values given by Edgar (Thesis, Mass. Inst. Tech., Boston, 1912) were interpolated directly from Table 18 and corrected to 1 atmos. H_2 at 25°. The correction of the results as given brings Brönsted's results into much better agreement among themselves and the corrected results agree quite closely with those of Edgar and of the present writers. These two corrected values are marked B^2 in the table.

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measurements were made at various temperatures. They have been interpolated for 25° and calculated to H_2 at 1 atmos. The results are given under B in Table II.

TABLE II.

Mol. fraction *N*.	E.	Author.
0.0000868	0.8243	B
0.0002710	0.7927	B
0.0009555	0.749	E
0.001121	0.7493	B
0.004987	0.7144	B
0.008825	0.688	E
0.008946	0.694	E
0.02175	0.6674	B[2]
0.04255	0.6373	B[2]
0.08010	0.5989	B
0.1110	0.5676	B
0.2014	0.4977	B

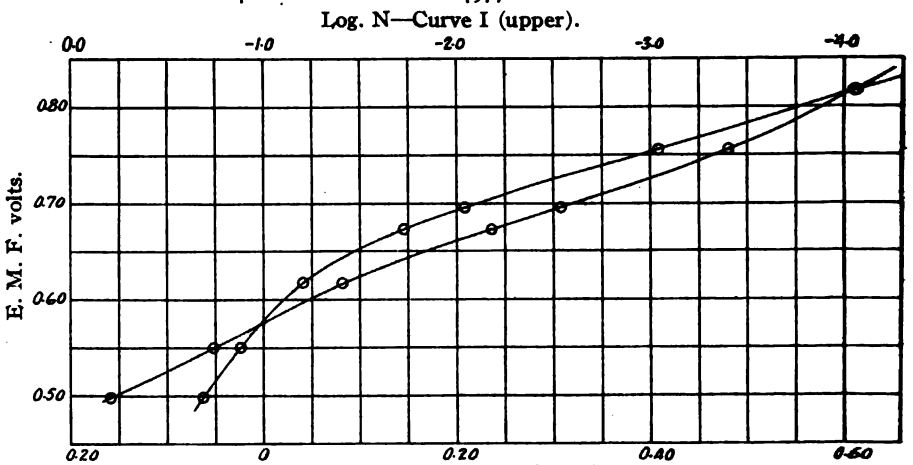

Fig. 1.

In Fig. 1 the values of the e. m. f. given in Tables I and II are plotted as ordinates. The abscissas are log. mol fraction for curve I and log. log. mol fraction for curve II. The experimental results of Randall and Cushman and of Lewis and Lacey all fall upon the smooth curve.[1] The values of the e. m. f. of the cell H_2, H_2SO_4(aq. N = x) Hg_2SO_4, Hg for round mol fractions[2] are given in the third column of Table III, and the corresponding value of the free energy ΔF (Equation 1) in the fourth column.

[1] The reliability of experimental data can often be inferred by plotting. In making interpolations or extrapolations it is important to choose the proper function of the variables. In Fig. 1, Curve I gives nearly a straight line for mol. fractions below 0.01 and Curve II for those above 0.05. In these regions the error of plotting is much reduced. The interpolated values of Table III were obtained by taking a mean of the interpolation by the aid of both functions. The error is not greater than 0.0002 volt.

[2] Intermediate values may be interpolated from the above table by assuming E or ΔF proportional to log. *N*.

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TABLE III.—FREE ENERGY OF THE REACTIONS $H_2 + Hg_2SO_4 = H_2SO_4(N = X) + 2Hg$, $2H^+ + SO_4^{--} = H_2SO_4(N = X)$.

N.	Log *N*.	E.	ΔF (Eq. 1).	ΔF (Eq. 4).
0.00009009	—4.0453	0.8160	—37657	—9382
0.0008999	—3.0458	0.7546	—34822	—6547
0.002	—2.6990	0.7343	—33888	—5613
0.005	—2.3010	0.7114	—32830	—4555
0.01	—2.0000	0.6929	—31977	—3702
0.015	—1.8239	0.6812	—31437	—3162
0.02	—1.6990	0.6720	—31010	—2735
0.03	—1.5229	0.6571	—30323	—2048
0.04	—1.3979	0.6442	—29730	—1455
0.05	—1.3010	0.6315	—29140	— 865
0.065	—1.1871	0.6145	—28360	— 85
0.08	—1.0969	0.5975	—27573	702
0.10	—1.0000	0.5770	—26630	1645
0.13	—0.8861	0.5495	—25360	2915
0.20	—0.6990	0.4985	—23003	5272

Lewis and Lacey[1] from a consideration of the data in very dilute solutions found for the cell

$$H_2, H^+(M) \,||\, SO_4^{--}(M), Hg_2SO_4, Hg \qquad (2)$$

corresponding to the reaction

$$H_2 + Hg_2SO_4 = 2H^+(M) + SO_4^{--}(M) + 2Hg; \qquad (3)$$

$E^\circ = 0.6127$, $\Delta F^\circ = -28275$ cal.

By subtracting Equation 1 from Equation 3 we obtain

$$2H^+ + SO_4^{--} = H_2SO_4(N = x);\ \Delta F = y \text{ (Table III, Col. 5).} \qquad (4)$$

These values of the free energy of formation from hypothetical molal hydrogen ion and sulfate ion are given in the last column of Table III. Since the free energy of formation[2] of H^+ is 0, the valves in the last column also give the free energy of the reaction

$$H_2 + SO_4^{--} + 2 \oplus = H_2SO_4(N = x). \qquad (5)$$

The free energy of formation of sulfate ion from the elements has not as yet been determined.

BERKELEY, CAL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF CALIFORNIA.]

TOLANE CHLORIDES FROM CALCIUM CARBIDE, CHLORINE AND BENZENE.

BY CLINTON DAVIDSON.

Received April 11, 1917.

Preparation of α-Tolane Dichloride.[3]—If well-ground calcium carbide

[1] Lewis and Lacey, THIS JOURNAL, **36**, 804 (1914).

[2] Lewis and Randall, *Ibid.*, **36**, 1969 (1914).

[3] References on tolane dichlorides, *Ber.*, **4**, 289, 379 (1871); **12**, 1973 (1879); **15**, 900 (1882); **17**, 835 (1884); **29**, 2906 (1896); **40**, 2994 (1907).

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is added to about four times its weight of benzene saturated with chlorine and cooled in a vessel of water, a reaction will soon set in. Heat is first developed and finally hydrogen chloride is given off. Since the reaction does not start for ten or fifteen minutes, it does not matter whether the chlorine is introduced before or after the calcium carbide. Enough heat is developed to raise the temperature of the benzene to its boiling point if the water used to cool it off is removed.

After the reaction has gone for some time, it will subside of its own accord even though an excess of chlorine still remains. This appears to be due to the formation of a layer of calcium chloride over the calcium carbide, thereby excluding the chlorine. The benzene solution can then be decanted from off the calcium carbide and placed in an ice chest overnight. The next morning a large crop of crystals of a chloro-hydrocarbon will be found on the walls of the vessel. They are a mixture of α- and β-tolane dichloride.

One sample thus obtained melted at 139–140°. After that same sample had been allowed to stand for three months (during the University summer vacation) the melting point had changed to 143°. α-Tolane dichloride melts at 143° and β-tolane dichloride melts at 63°. A mixture of the two isomerides had been produced and had slowly been converted into the more stable α-modification. It was afterward found that the same reaction could be completed in a week by allowing a saturated benzene solution of the two to stand on a steam bath at 100° during that time.

In preparing these compounds certain precautions must be observed. The benzene used must be free from its higher homologs; otherwise a hopeless mixture will be obtained. For the production of pure α-tolane dichloride, the temperature of the reaction should be kept as low as possible to avoid addition of chlorine. But the most important precaution of all is to have the calcium carbide used, free from iron compounds. If much iron is present the benzene solution will become red in color instead of remaining yellow with chlorine and the reaction will not come to an end with an excess of chlorine still present. Instead the iron causes direct substitution of chlorine in the benzene ring so that the product obtained is a mixture of chlorine derivatives of tolane and benzene. If no iron is present, the benzene will remain yellow with chlorine for days without a reaction taking place between them.

Calc. for α-tolane dichloride: Cl: 28.5%. Found: 29.9, 30.0%.

The melting point was correct and not near that of any other compound that might be produced. A molecular-weight determination, obtained from the lowering produced upon the freezing point of benzene, was 230 ± 4%. Theory requires 249. Alcoholic potash removed all of the chlorine from it, thus indicating the absence of any chlorine in the

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benzene rings. Sodium in alcohol reduced it to dibenzyl. The vapors from it cause the eyes to burn just as does benzal chloride.

Properties of α-Tolane Dichloride.—It is a colorless crystallin solid with a specific gravity of 1.78. If it is slowly crystallized from benzene, crystals of the monoclinic system are obtained. Under atmospheric pressure it boils at 275–278° with slow blackening due to slight decomposition. However, it may be distilled over as white as paraffin if it is cooled quickly after condensation, its boiling point still remaining unchanged.

Preparation of Tolane Tetrachloride.[1]—Referring back to the original reaction; if the decanted benzene, containing chlorine and the two tolane dichlorides, is not cooled at once but is concentrated by boiling on a steam bath for several days until the boiling point reaches 100° and is then cooled, the compound that crystallizes out will have absorbed chlorine and its melting point will have decreased or increased, depending upon the amount of chlorine absorbed. Tolane tetrachloride is the compound produced by this absorption. Under these circumstances its production in the pure state does not seem to be possible. Better results were obtained when the pure α-tolane dichloride was chlorinated at its melting point. A product was obtained that melted at 161°. Tolane tetrachloride melts at 163°.

In the original preparation, if the benzene is replaced with toluene, the reaction goes on with even more ease than before, producing an oil that does not solidify at 0° but that boils at 238–242°. It is probably a mixture of the isomerides having the formula $CH_3.C_6H_4.CCl : CCl.C_6H_4.CH_3$.

The discovery of this reaction resulted from the examination of the action of chlorine upon hot calcium carbide. With great difficulty a small amount of gas was obtained from the latter compound which seemed to be dichloroacetylene. It was spontaneously combustible and decomposable after decomposition had once begun; a thing to be expected considering the properties of dibromo-acetylene.[2] Hoping to obtain a derivative of it, the author decided to try the reaction in the presence of some compound with which it might react. Benzene was chosen for this purpose. The resulting tolane chlorides may therefore be produced as indicated by the following equations:

$$CaC_2 + 2Cl_2 \longrightarrow CaCl_2 + Cl.C : C.Cl$$

$$Cl.C : C.Cl + 2C_6H_6 \longrightarrow C_6H_5.C : C.C_6H_5 + 2HCl$$

$$C_6H_5.C : C.C_6H_5 + Cl_2 \longrightarrow C_6H_5.CCl : CCl.C_6H_5, \text{ and}$$

$$C_6H_5.CCl : CCl.C_6H_5 + Cl_2 \longrightarrow C_6H_5.CCl_2.CCl_2.C_6H_5$$

[1] Cf., *Ber.*, **12**, 1971 (1879); **15**, 901 (1882); **17**, 833 (1884); **40**, 2994 (1907); *Chem. Zentr.*, **1907**, 2, 1069.

[2] *Chem. Zentr.*, **1903**, 2, 102, 551; *Compt. rend.*, **136**, 1333 (1903); **137**, 55 (1903).

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Thus, although the existence of dichloro-acetylene has not been proven, it existence seems possible.

BERKELEY, CALIF.

THE LIMITS OF ACCURACY OF HOLLEMAN'S METHOD OF DETERMINING THE COMPOSITION OF A MIXTURE OF TWO OR THREE ISOMERS.

BY JOSEPH B. NICHOLS.

Received September 18, 1917.

Holleman[1] gives a method for the quantitative determination of three isomers, depending upon the freezing point. This method is a special application of Bakhuis Roozebooms general method of determing the freezing points of mixed crystals, etc.[2] The purpose of the present experiments is to discover the limits of accuracy of this method, together with the details of the manipulation. While Holleman shows the applications of his method to many compounds, he says nothing of its limit of accuracy. A short résumé of the method will first be given; for a more extended description the reader is referred to Holleman's book, and to the references given therein. It is plain that if the method furnishes accurate enough results, it will save much tedious work formerly required in investigations of isomers of this character, in separating the products to determine the result.

If two isomers are melted together and allowed to cool, unless they form a eutectic mixture, one of the isomers will start to solidify at a definite temperature, depending on the proportion of the substances. This isomer will freeze out until the eutectic point is reached, when the whole mass will solidify together. In this way, after determining a curve for the freezing points of different mixtures of the two substances, the constitution of a binary mixture can be determined from the position on the curve of the freezing point. This curve has two branches, dropping from the freezing point of one pure isomer to the eutectic, and then rising to the freezing point of the second substance. It is always possible, however, to find on what branch of the curve a given point lies, by adding a weighed portion of one of the isomers to the mixture, and observing the position of the freezing point for the resulting mixture.

In most compounds produced by the addition of substituents to the benzene nucleus, two of the isomers occur chiefly, while the third is found in small porportions—from a mere trace to 8 or 10%. In some cases only one isomer is obtained in quantity; this, however, necessitates only changes

[1] "Die direkte Einfuhrung von Substituenten in den Benzolkern" (Veit & Co., 1910).

[2] *Z. physik. Chem.*, **30**, 386 (1899). Reference may be made to Roozeboom's "Die Heterogene gleichgewichte von Standpunkte der Phasenlehre" Vol. II, 1904 for further information on the general theory.

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in the details of the method. The effect of the third isomer is to change the position of the freezing point, and also to lower the eutectic. For the small amount which usually occurs, the amount of lowering of the eutectic is directly proportional to the quantity of the third substance present—that is, the curve of the lowering may be considered as a straight line. For arbitrary mixtures of three isomers of any proportion, Holleman gives two methods, by which a quantitative estimation may be made without first determining the entire freezing-point surface of the ternary mixture. These methods are not considered here, but would obviously have about the same degree of accuracy.

The method recommended by Holleman is as follows: The mixture, after suitable purification, containing the three isomers and free from all other substances, is placed in a test tube and melted, and the freezing point approximately determined with an ordinary thermometer. It is then heated to a few degrees above the melting point, and placed inside a second test tube large enough to furnish a small air space. This second tube is immersed in a suitable bath, furnished with a stirrer; or for lower temperatures, in a Dewar flask with a suitable cooling mixture. This bath is provided with a thermometer and is kept from 5 to 10°, according to circumstances, below the temperature of the substance in the tube. A thermometer graduated to 0.10 is immersed in the substance, and is used to stir the mixture. The temperature drops at the same rate as the bath, but is a little higher, as mentioned above. The mixture supercools a little, and then, when the first isomer commences to solidify latent heat is liberated and the temperature rises. The highest point so reached is the primary freezing point: in a binary mixture this is sufficient to determine the composition. The rate of cooling must not be too rapid. It will be noticed that the procedure is essentially the same as that used in determing the lowering of the freezing point by Beckmann's method.

The primary point is determined two or three times and the results averaged together. Then the mixture is allowed to cool, without further stirring, until the second isomer also beings to solidify. This gives the secondary point, or, in a binary mixture, is the eutectic. Three or four determinations are made of this point, also.

The results are calculated by taking a mixture of the two substances appearing in the largest proportions, and observing the lowering of the primary and secondary points on adding a given quantity of the third isomer. A carefully weighed amount of the third isomer is then added to the sample, and the lowering of the two points observed. A simple proportion between the per cent. added and the lowering of the secondary point produced gives the percentage of the third isomer, and subtracting the lowering produced by this amount from the primary point gives the percentage of the second isomer.

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In the experimental work, nitraniline was chosen as the substance. The freezing points of the three isomers lie far apart, *p* — 166.99°, *m* — 109.0, *o*—71.5. Also, the application of this method to nitraniline is not mentioned by Holleman.

A curve was constructed from the freezing points obtained from mixtures of *m*- and *p*-nitraniline as given below.

Temperature.	*m* %.	*p* %.
146.99	00.00	100.00
145.66	1.47	96.53
144.03	3.91	96.09
143.07	5.55	94.45
141.27	8.34	91.66
140.01	10.07	89.93
135.97	15.44	84.56
134.07	17.66	82.34
126.18	26.44	73.56
117.53	34.44	65.56
110.87	40.23	59.77
97.21	48.90	51.10

This curve, as plotted, was very regular. The difficulty of obtaining consistent points is greater when more than 35% of *m*-nitraniline is present, but by adding a weighed amount of *p*-nitraniline, the percentage of *m* may be made as small as desired. The curve also exhibits irregularities when less than 10% *m*.

After plotting the curve, various mixtures were taken, and the percentages given by the position of the freezing point on the curve compared with the true proportions.

BINARY MIXTURES.

	Temperature.	% *m* with *p*. From curve.	% *m* with *p*. True %.
A	114.43	37.45	37.55
B	119.09	33.48	33.66
C	140.12	9.99	9.12
D	126.74	25.77	25.82
E	131.39	20.80	20.86
F	133.59	18.27	18.24

It will be noticed that the results obtained for A and B are not so close as those for D, E and F. These latter points are very close; this portion of the curve seems to give very accurate results. Also, C is still less accurate; it was noticed above that the portion of the curve below 10% of *m* is very irregular.

The chief points to be noted in the manipulation are that it is best to stir the substance very little until it has supercooled and the temperature has started to rise, when it must be stirred continuously until the point is reached. The stirring, however, must be regular, but not too vigorous. The difference in temperature between the bath and the substance must

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not be too great, though a few degrees' difference in the temperature of the bath does not affect the freezing point of the mixture appreciably, in the successive determinations. The substance must not be cooled too rapidly. It is very necessary that the substance should be thoroughly melted before taking the freezing points, as a few small crystals remaining solid when the substance is first placed in the bath will greatly affect the result. This precaution is even more important in determining the secondary points; if all the substance is not melted, the point obtained may be two or three degrees lower than it should be. In taking the secondary point, it is also necessary that the mixture be continually stirred until the primary point is reached, and that it then be allowed to cool with no further stirring. Failure to observe these conditions gives successive points varying very widely.

To test the accuracy of the method for three isomers, it is necessary to determine the eutectic point for the binary mixture, and then adding small amounts of *o*-nitraniline to observe the lowering produced. The results of two such experiments are given below.

A. For 20.86% *m* with *p*. Eutectic is 86.63°.

	% *o*.	Temperature.	Lowering.	For 1% lowering is
1	1.76	82.21	4.42	2.51°
2	3.99	76.44	10.19	2.55
3	6.96	68.27	18.36	2.63
4	8.45	62.59	24.04	2.84
5	11.22	57.04	29.59	2.64

B. For 24.55% *m* with *p*. Eutectic is 86.74°.

1	0.86	84.75	1.99	2.31
2	2.78	80.44	6.30	2.26
3	7.33	68.77	17.97	2.45

It is also necessary to observe the effect of the third isomer on the primary point. This is done by observing how closely the freezing point for a given percentage of *o*- plus *m*-nitraniline corresponded to the point for a like percentage of *m*-nitraniline.

Temperature.	Corresponds to % *m*.	% *o* plus *m*.	% *o*.
130.03	22.31	22.29	4.84
129.52	22.90	22.23	5.96
129.57	29.18	29.74	11.22

It will be observed that for 5% or less of *o*—the lowering of both primary and secondary points gives very close results, diverging more widely for larger amounts. However, for as high as 10% of the third isomer it is evident that in the case of nitraniline, at least, the accuracy of the method is all that could be desired.

The author is indebted to Professor H. C. Biddle, University of California, for assistance and supervision in the above work.

BERKELEY, CALIF.

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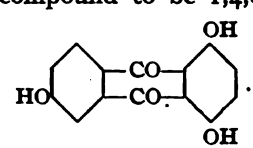
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WESLEYAN UNIVERSITY.]

1,4,6-TRIHYDROXYANTHRAQUINONE.

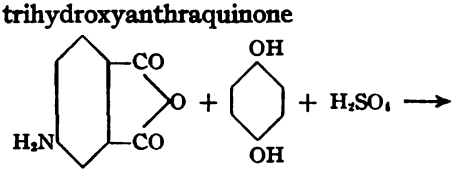
BY M. L. CROSSLEY.

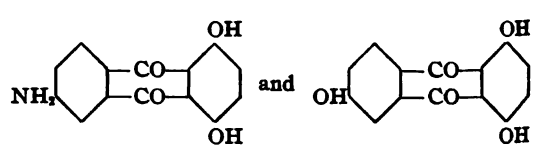
Received November 14, 1917.

Of the several possible trihydroxyanthraquinones, seven isomers, the 1,2,3–, 1,2,4–, 1,2,5–, 1,2,6–, 1,2,7–, 1,2,8–, and 1,4,8–, have been discovered and studied prior to this synthesis. The purpose of this research was to prepare 6-amino-1,4-dihydroxyanthraquinone by condensing 4-aminophthalic anhydride with hydroquinone. The result of the condensation was a mixture of two substances whose sodium salts differ in color and solubility. The more soluble of the two is blue-violet and the other is red-brown. On acidification of the blue-violet sodium salt a product is obtained which when purified analyzes for $C_{14}H_8O_5$. It is a reddish brown powder which is slightly soluble in boiling water, giving a solution which is yellowish red. It does not crystallize from its water solution. It is quite soluble in glacial acetic acid, ethyl alcohol, methyl alcohol, ether, chloroform, and nitrobenzene. It is sparingly soluble in benzene. It is best purified by precipitating it with water from a glacial acetic acid solution and subsequently crystallizing from nitrobenzene. It dissolves readily in alkalies giving blue-violet salts which are quite soluble in water. It is not important as a mordant dye. It gives the anthranol and picrate tests for the anthraquinone molecule. The behavior of the substance and the synthesis prove the compound to be 1,4,6-trihydroxyanthraquinone



The aminophthalic anhydride and hydroquinone condense to give the aminodihydroxyanthraquinone, a part of which is converted into the trihydroxyanthraquinone





The less soluble sodium salt obtained from the reaction mixture contains nitrogen and appears to be the sodium derivative of aminodihydroxyanthraquinone. Its water solution is reddish brown. By neutralizing the alkaline solution a dark blackish product is precipitated. This is

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not very soluble in organic solvents and does not crystallize. Its nitrogen content agrees with that calculated for $C_{14}H_9O_4N$.

Experimental Part.

4-Aminophthalic Anhydride.—Phthalic anhydride was nitrated as described by Bogert and Boroschek[1] and the resulting 3- and 4-nitro acids were roughly separated by crystallization from water and then the crude 4-nitrophthalic acid was converted into the corresponding methylphthalate by the method of Bogert and Renshaw.[2] The 4-nitrodimethylphthalate was then reduced to the corresponding amino compound by the method of Baeyer.[3] The ester was saponified by boiling it with an alcohol solution of sodium ethylate and the sodium salt was subsequently decomposed with hydrochloric acid to give the 4-aminophthalic acid. This acid was then dehydrated by the method of Bogert and Renshaw[4] and a fair yield of the anhydride thus obtained.

1,4,6-Trihydroxyanthraquinone.—A mixture of 5 g. of 4-aminophthalic anhydride, 3 g. of hydroquinone, and 40 g. of concentrated sulfuric acid was heated in a round flask in an oil bath at 170° for two hours. The temperature was raised to 190° and maintained at this point for one hour. The reaction product was then poured into water and the mixture stirred thoroughly. It was filtered on a Buechner funnel and washed with water until free from acid. It was extracted with a cold 10% solution of sodium hydroxide and a violet-blue solution obtained. This was acidified with hydrochloric acid. A reddish brown substance separated from the acid solution. It was filtered and washed with water until free of acid. The product was then dissolved in glacial acetic acid and again reprecipitated by dilution with water. It was filtered and then crystallized from nitrobenzene. It is nitrogen-free and does not melt below 300°. The yield of the pure product was 1.9 g.

Calc. for $C_{14}H_8O_5$: C, 65.62; H, 3.13; O, 31.25. Found: C, 64.84; H, 3.00; O, 32.16.

The residue left from the extraction with sodium hydroxide was boiled with sodium hydroxide and gave a dark brown solution from which a blackish substance containing nitrogen was precipitated by acid. This product was not obtained in a pure condition but its properties suggest that it is an aminohydroxyanthraquinone. It gives positive tests for amino, hydroxyl, and anthraquinone groups.

Conclusions.

By the condensation of 4-aminophthalic anhydride with hydroquinone a mixture of two substances is obtained. One of these proves to be 1,4,6-

[1] THIS JOURNAL, 23, 740 (1905).
[2] *Ibid.*, 28, 617 (1906).
[3] *Ber.*, 10, 125, 1079 (1877).
[4] *Loc. cit.*

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trihydroxyanthraquinone and the other seems to be an aminohydroxyanthraquinone, although its purity has not been established with absolute certainty.

This new trihydroxyanthraquinone is not a mordant dye of importance.

By the method employed the yield of the trihydroxyanthraquinone was about 24% of theory.

MIDDLETOWN, CONN.

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

THE BROMINATION OF *p*-NITROTOLUENE.

BY J. F. BREWSTER.

Received November 15, 1917.

Reid[1] has recently made a study of the reaction between *p*-nitrobenzyl bromide and the alkali salts of several organic acids and phenols in which there is formed, respectively, the corresponding *p*-nitrobenzyl ester or ether. In the case of many of the acids and phenols Reid found that the products were obtained in good yield, were readily purified, and, having sharp melting points, the reaction could be recommended as a method of identification.

Having occasion to use Reid's method, the author set about preparing a supply of the bromide, first by heating *p*-nitrotoluene with bromine in sealed tubes as Reid recommends. Frequent breakage, however, due to the poor quality of tubing then at hand, led to a search for some other way to prepare the bromide.

A much easier and more satisfactory method has been found and although there is very little involved therein that is not well known, it was thought worth while to record the procedure as the product itself is of great usefulness.

The method of bromination consists in adding a carbon tetrachloride solution of the calculated quantity of bromine to a boiling carbon tetrachloride solution of *p*-nitrotoluene, containing iodine as catalyzer, in direct sunlight. The reaction proceeds smoothly and rapidly, the actual bromination can be finished in 30 to 60 minutes, and the product, ready for drying, can be obtained in a total time of two hours or less. The yields are from 60 to 71% of the theoretical.

In attempts by this method to prepare *p*-nitrobenzylidene bromide, the second molecule of bromine reacted readily. However, the yield, after necessary recrystallizations for purification, was very small. The third molecule of bromine did not react.

Experimental.

Ten grams of *p*-nitrotoluene contained in a flat-bottomed flask were

[1] Reid, E. Emmet, THIS JOURNAL, 39, 124, 304 (1917).

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dissolved in 100 cc. carbon tetrachloride and a small crystal of iodine was added. The flask, fitted by ground joint to a reflux condenser, was placed on an electric hot plate in direct sunlight and the contents allowed to boil. 11.7 g. (1 mol) bromine dissolved in 50 cc. carbon tetrachloride were introduced in small quantities at a time by means of a separatory funnel whose stem was sealed into the side of the lower part of the condenser tube. Rapid evolution of hydrogen bromide began at once. This was absorbed by water contained in Folin bulbs fitted to the upper end of the condenser.[1] When all the bromine had been used up the flask was detached after cooling and the carbon tetrachloride distilled off. On cooling, the oily residue at the botton of the flask crystallized in a solid mass. This was dissolved by boiling in 95% alcohol and filtered. The filtrate was rapidly cooled and allowed to stand a short time at 0°. The fine crystals were filtered by suction and dried in the air overnight. The yield was 11.2 grams, or 71% of the theoretical. Melting point 99–100°, uncorrected.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF PITTSBURGH.]

PHTHALIC ACID DERIVATIVES: CONSTITUTION AND COLOR. XII.[2] TETRACHLOROPHTHALOXIME AND SOME OF ITS DERIVATIVES.

BY DAVID S. PRATT AND CHARLOTTE H. MILLER.

Received November 16, 1917.

The study of phthalic acid derivatives resulting from replacement in various positions in the molecule and the effects thereby on color has been continued. The present paper considers certain derivatives of tetrachlorophthalic anhydride obtained after one oxygen atom has been replaced by the NOH radical. The reaction is brought about readily by treating tetrachlorophthalic anhydride with an aqueous solution of hydroxylamine. The particular interest in the resulting oxime lies in the proximity effects taking place between the hydroxyl group and the nucleus. This effect becomes very marked on salt formation when it is evidenced to the eye by a vivid red color.

Unhalogenated phthaloxime was found to exist in two modifications, one colorless, and the other canary yellow,[3] but neither Orndorff and

[1] The apparatus can be simplified by covering the carbon tetrachloride solution in the flask with a little water. This absorbs all hydrogen bromide. If the bromide is introduced by a separatory funnel the tip of whose stem extends down the condenser tube to the point where the vapors condense, there is no loss of bromine whatever and the experiment can be conducted in the open laboratory. The yields by this method are somewhat lower.

[2] THIS JOURNAL, 40, 254 (1918).

[3] Orndorff and Pratt, *Am. Chem. J.*, 47, 90 (1912).

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Nichols,[1] who first prepared the tetrachloro derivative, nor the authors, have observed a similar phenomenon in this case. We have made the oxime under a variety of conditions but always obtained a pale yellow form.

The oxime readily yields a red silver salt from which a variety of ethers were prepared. It should be noted that whereas the oxime itself is faintly yellow the derivatives are all without color. Yellow phthaloxime did give yellow compounds throughout the series as far as developed and such would be expected from the tetrachloro-oxime if it corresponded to the colored isomer. The colorless ethers here reported lead us to believe that the tetrachloro-phthaloxime itself, although yellow, corresponds to the colorless phthaloxime, and that the higher colored form has not yet been obtained.

The new derivatives here reported did show, however, new and interesting cases of dimorphism which establish their position in relation to the anil derivatives already discussed.[2] These anils result from a series of steps in the type reaction between phthalic anhydride and primary aromatic amines and are considered as derived from phthalimide by the replacement of hydrogen by phenyl, etc., whereas in the oxime this hydrogen is replaced by hydroxyl. Dimorphism in phthaloxime derivatives had not been observed before, and even in these tetrachloro compounds it was not always possible to obtain two forms. In many cases, however, an individual product could be isolated both as long cotton-like needles and as compact stubby prisms, each form readily convertible into the other.

The methyl ether from silver salt and methyl iodide could be obtained only in the form of compact colorless blades, but the corresponding ethyl ether shows very distinctly this unusual property. When a saturated solution in methyl alcohol is cooled rapidly the ether crystallizes out readily in exceedingly fine hair-like clusters resembling wisps of cotton. These crystals, on standing some hours in the mother liquor, go over gradually into colorless, thick prisms so entirely distinct as to suggest a different substance. Both forms have the same melting point or very nearly so, and show no different mixed melting point.

The isopropyl ether exists both as very thin, gleaming plates and as heavy prisms. The benzyl ether could be obtained only as cotton-like wisps, while the benzoate gave nacreous diamond-shaped plates and prisms. Similarly, the allyl ether gave both coarse prisms and fine needles.

This property of dimorphism appears to be particularly favored by the presence of the four chlorine atoms in the molecule. It has never been observed in the phthaloxime series and was not found with correspond-

[1] *Am. Chem. J.*, **48**, 495 (1912).

[2] THIS JOURNAL, **40**, 203 (1918).

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ing tetraiodo compounds. In all cases where two forms were obtained there appeared to be no other differences with the possible exception of melting points. These sometimes appeared to differ slightly but rapid conversion of the less stable into the more stable form near the melting point made analytical differentiation impossible.

The easy conversion of one form into the other without change in weight, often so rapidly that the transformation could be followed under the microscope, leads us to consider the phenomenon one of dimorphism probably due to different arrangements of identical molecules in the crystals. The dimorphism, therefore, is entirely analogous to that reported for tetrachlorophthal-*p*-tolil *q. v.*

Tetrachlorophthalyl phenylhydrazone was prepared from anhydride and phenylhydrazine for purposes of comparison. As ordinarily obtained either from glacial acetic acid or alcohol, it forms long, curving, orange needles tending to cluster in sheaves. It was observed on examining these crystals under the microscope that very rapid cooling of the acetic acid solution gave thin four-sided lemon-yellow plates if fairly large size. These plates show interference colors as they float in the mother liquor and could not be confused with the orange needles. The plates go over into the stable needles instantly when moistened with alcohol. It was not possible to obtain the unstable form free from the needles, as the same change takes place even in the dry crystals.

The dimorphism here is analogous to that observed by Dunlap[1] and studied by Chattaway.[2] Both forms probably have the symmetrical structure, $C_6Cl_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right.>N.NHC_6H_5$ and are to be considered as derived from the oxime by the replacement of hydroxyl by the anilino group.

The various new derivatives here reported will be considered from the theoretical standpoint of constitution and color when necessary absorption spectra apparatus becomes available.

Experimental.

Tetrachlorophthaloxime.—57.0 g. of tetrachlorophthalic anhydride were ground to pass an 80-mesh sieve, an important factor in securing good yields as otherwise considerable amounts of material remain unacted upon. 17.4 g. of hydroxylamine hydrochloride and 17.3 g. of sodium carbonate were dissolved in 200 cc. of water and the finely ground anhydride added. The suspension was stirred about ten minutes at room temperature, then placed in a bath of boiling water for 4 hours. It was stirred occasionally during the heating, finely acidified with dilute hydrochloric acid and filtered. The product was washed with hot water until

[1] THIS JOURNAL, 27, 1091 (1905).

[2] *J. Chem. Soc.*, 99, 2253 (1911).

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free from acid. Yield, 57 g. or 95% theoretical. The hydrate so obtained was recrystallized from methyl alcohol and acetone, dried to constant weight at 120° and analyzed.

Subst. (I) 0.1350, (II) 0.1227; cc. 0.1 *N* $AgNO_3$, (I) 18.03, (II) 16.34.
Calc. for $C_8HO_3NCl_4$: Cl, 47.14%. Found: (I) 47.38, (II) 47.22.

Chlorine was determined by the lime combustion method.

Silver Salt of Tetrachlorophthaloxime.—The silver salt was prepared by dissolving the oxime in boiling methyl alcohol and adding a solution containing four equivalents of silver nitrate in water and just enough ammonia to redissolve the silver oxide. The silver salt precipitated as a gelatinous, red mass. It was warmed 15 minutes on a water bath to insure complete reaction, filtered and washed free from excess silver with methyl alcohol. Yield, theoretical. It was not possible to remove all adsorbed silver nitrate as shown by analysis. This was made by treating a sample of the dry salt with dilute nitric acid in the cold, letting it stand overnight, and titrating the silver nitrate so formed with standard ammonium thiocyanate.

Subst. (I) 0.1561, (II) 0.1321; cc. 0.1 *N* NH_4SCN, (I) 4.43, (II) 3.84.
Calc. for $C_8O_3NCl_4Ag$: Ag, 26.46%. Found: (I) 30.66, (II) 31.36.

Methyl Ether—5.0 g. of dry silver salt were suspended in ether containing 3 cc. of methyl iodide and boiled gently with a reflux condenser for 48 hours. The ether was recrystallized from alcohol in the form of shining, colorless blades, melting at 206° (corr.). No other form was observed.

Subst. (I) 0.0493, (II) 0.0896; cc. 0.1 *N* $AgNO_3$, (I) 6.25, (II) 11.32.
Calc. for $C_9H_3O_3NCl_4$: Cl, 45.04%. Found: (I) 44.95, (II) 44.80.

Ethyl Ether.—The ethyl ether similarly made was recrystallized from ether by adding ligroin, followed by slow distillation. It was thus obtained as coarse, colorless prisms, generally in star-like clusters and melting at 160° (corr.). The ethyl ether dissolves readily in boiling methyl or ethyl alcohol, and deposits, on rapid cooling, in abundant, fine, hair-like crystals which mat together like cotton. Brief standing in the mother liquor converts this unstable form into prisms, but it is quite stable when dry.

Subst. (I) 0.0929, (II) 0.1168; cc. 0.1 *N* $AgNO_3$, (I) 11.26, (II) 14.27.
Calc. for $C_{10}H_5O_3NCl_4$: Cl, 43.12%. Found: (I) 43.06, (II) 43.32.

Isopropyl Ether.—The isopropyl ether was extracted from resulting silver iodide with boiling chloroform in which it is very soluble. Methyl alcohol was then added slowly to abundant crystallization. The isopropyl ether forms either very thin, glistening plates or clusters of coarse prisms, the latter apparently being the stable form. Both modifications are colorless and melt at 146° (corr.).

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Subst. (I) 0.0934, (II) 0.0997; cc. 0.1 N $AgNO_3$. (I) 10.89, (II) 11.70.
Calc. for $C_{11}H_7O_3NCl_4$: Cl, 41.35%. Found: (I) 41.34, (II) 41.61.

Isoamyl Ether.—Recrystallized from chloroform-alcohol mixture by sudden cooling it forms fine hair-like crystals which go over into the short prism form on standing. It melts at 244° (corr.).

Subst. (I) 0.0852, (II) 0.0587; cc. 0.1 N $AgNO_3$. (I) 9.18, (II) 5.99.
Calc. for $C_{13}H_{11}O_3NCl_4$: Cl, 38.23%. Found: (I) 38.21, (II) 38.84.

Allyl Ether.—The allyl ether was prepared from freshly distilled allyl iodide and silver salt suspended in ether and boiled 7 hours. The solvent was distilled off and the residue extracted with boiling chloroform. The product was recrystallized from chloroform and glacial acetic acid. Rapid cooling of the solution sometimes gave the hair-like form, but as a rule clusters of short, stubby prisms were obtained. They are without color and melt at 186° (corr.).

Subst. (I) 0.1138, (II) 0.1048; cc. 0.1 N $AgNO_3$. (I) 13.27, (II) 12.38.
Calc. for $C_{11}H_8O_3NCl_4$: Cl, 41.60%. Found: (I) 41.50, (II) 41.89.

Benzyl Ether.—The benzyl ether was made by boiling the silver salt with an excess of benzyl chloride until the red color disappeared. The solution was then filtered hot and alcohol added to precipitation. The substance was recrystallized from acetone and alcohol. It was obtained only in the colorless cotton-like form, melting at 192° (corr.).

Subst. (I) 0.1455, (II) 0.1337; cc. 0.1 N $AgNO_3$. (I) 14.07, (II) 13.68.
Calc. for $C_{15}H_7O_3NCl_4$: Cl, 36.27%. Found: (I) 36.48, (II) 36.29.

Acetate.—5.0 g. of tetrachlorophthaloxime and 10 cc. of acetic anhydride were boiled gently until dissolved, cooled and poured into about 30 cc. of absolute alcohol. The acetate was filtered off, washed with alcohol, and recrystallized from ethyl ether. Yield, practically quantitative. The substance was obtained only in colorless needles melting at 179.5° (corr.). Nitrogen was determined by the Kjeldahl method after thorough reduction with zinc dust and dilute sulfuric acid.

Subst. (I) 0.1148, (II) 0.1069; cc. 0.1 N $AgNO_3$. (I) 13.40, (II) 12.55.
Calc. for $C_{10}H_5O_4NCl_4$: Cl, 41.36%. Found: (I) 41.39, (II) 41.60.
Subst. (III) 0.2212, (IV) 0.2433; cc. 0.1 N HCl. (III) 6.56, (IV) 7.11.
Calc. for $C_{10}H_5O_4NCl_4$: N, 4.08%. Found: (III) 4.16, (IV) 4.09.

Benzoate.—5.0 g. of silver salt suspended in ether were treated at room temperature with 5 cc. of benzoyl chloride. The reaction takes place at once with the evolution of considerable heat. The solvent was distilled off and excess benzoyl chloride removed by boiling the residue with methyl alcohol. The benzoate, in about 80% yield, was recrystallized by rapid cooling from chloroform as pearly four-sided diamond plates. When the plates are moistened with methyl alcohol they are converted into stubby prisms. The change takes with sufficient rapidity to show

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clearly under the microscope. Both forms are colorless and melt at 210° (corr.).

Subst. (I) 0.1705, (II) 0.1000; cc. 0.1 *N* $AgNO_3$. (I) 16.87, (II) 9.88.
Calc. for $C_{18}H_8O_4NCl_4$: Cl, 35.02%. Found: (I) 35.08, (II) 35.04.

Tetrachlorophthalyl Phenyl Hydrazone.—5.0 g. of tetrachlorophthalic anhydride in 200 cc. glacial acetic acid were added to 2 cc. of phenylhydrazine in 25 cc. of the same solvent and the mixture boiled for 15 minutes. The first reaction is the formation of anilino-tetrachloro-phthalamic acid, but this readily splits off a molecule of water during the heating and gives orange needles of the phenylhydrazone. The product was recrystallized from glacial acetic acid and from alcohol. The yellow plate modification was obtained by very rapid cooling of an acetic acid solution. It is unstable and rapidly reverts to the orange needles. The substance melts at 287° (corr.).

Subst. (I) 0.0793, (II) 0.0977; cc. 0.1 *N* $AgNO_3$. (I) 8.23, (II) 10.37.
Calc. for $C_{14}H_8O_2N_2Cl_4$: Cl, 37.73%. Found: (I) 37.75, (II) 37.64.

PITTSBURGH, PA.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF PITTSBURGH.]

PHTHALIC ACID DERIVATIVES: CONSTITUTION AND COLOR. XIII.[1] TETRAIODOPHTHALOXIME AND SOME OF ITS DERIVATIVES.

BY DAVID S. PRATT AND THOMAS B. DOWNEY.

Received November 16, 1917.

The large proportion of iodine in tetraiodophthalic anhydride and its sulfur yellow color, probably due to the proximity effects of the unsaturated halogen atoms, made it desirable to prepare the corresponding oxime. The study of substituted phthalic acid compounds was, therefore, made to include the material reported in this paper. Tetraiodophthalic anhydride represents the maximum molecular weight possible in a halogenated ring, the presence of the most unsaturated halogen atoms, and the greatest effect obtainable by this type of substitution.

Tetraiodophthaloxime was obtained without difficulty. 50.0 g. of tetraiodophthalic anhydride,[2] ground to a fine powder, were added to a solution of 6.4 g. hydroxylamine sulfate and 6.6 g. sodium bicarbonate in 250 cc. water. The suspension was warmed in a boiling water bath for 2 hours with occasional stirring, finally acidified with hydrochloric acid to break up any oxime salt, and filtered. The product was washed thoroughly with hot water until free from inorganic matter and dried. Yield, 52.0 g. crude oxime or 93% theoretical.

The impure product was recrystallized until pure from glacial acetic

[1] THIS JOURNAL, 40, 407 (1918).
[2] Pratt and Shupp, *Ibid.*, 40, 254 (1918).

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acid and obtained as long, lemon yellow needles which decompose without melting. It is slightly soluble in hot acetic acid, less in alcohol and other organic solvents. No other form was obtained, although many attempts were made under a variety of conditions.[1] Iodine was determined by the lime combustion method.

Subst. (I) 0.4345, (II) 0.4638; cc. 0.1 *N* $AgNO_3$. (I) 26.10, (II) 27.84.
Calc. for $C_8HO_3NI_4$: I, 76.14%. Found: (I) 76.23, (II) 76.18.

The very marked yellow color of the anhydride itself makes it probable, if not certain, that the modification of this oxime corresponding to the colorless phthaloxime would be yellow. The more highly colored form analogous to yellow phthaloxime would then be yellow or orange. It could not be determined, therefore, which of the two possible modifications were obtained. The slight solubility of tetraiodophthaloxime in all solvents may have been responsible for the non-appearance of a pseudomorphic modification.

The salts of tetraiodophthaloxime are red in color, and are insoluble in all solvents. Aqueous ammonia precipitated its salt from an alcoholic solution of the oxime, but it lost ammonia on drying. A weighed sample of oxime in a porcelain boat was exposed to dry ammonia gas for 2 weeks without gain in weight or change in color. This is remarkable as unhalogenated phthaloxime readily absorbs one molecule of ammonia giving the salt, and the iodine derivative would be expected to show stronger acidic properties.

Silver Salt.—The silver salt was made by adding a hot solution of silver nitrate in just enough ammonium hydroxide to redissolve the oxide to a hot alcoholic solution of tetraiodophthaloxime. The salt precipitated at once in red, flocculent form. It was filtered off, washed free from excess silver and dried at 100°. Analysis was made by treating with dilute nitric acid and titrating with standard ammonium thiocyanate.

Subst. (I) 0.2325, (II) 0.2933; cc. 0.1 *N* NH_4SCN. (I) 2.60, (II) 3.33.
Calc. for $C_8O_3NI_4Ag$: Ag, 13.95%. Found: (I) 12.07, (II) 12.18.

Methyl Ether.—The methyl ether was prepared by suspending 10 g. of dry silver salt in 100 cc. ethyl ether containing 5 cc. methyl iodide. The reaction proceeded slowly at room temperature and was complete within 24 hours. The mixture of silver iodide and methyl ether was filtered off and extracted with 4 liters of boiling glacial acetic acid. 6 g. of canary yellow needles were obtained representing a yield of 70 per cent. The ether does not melt.

Subst. (I) 0.5352, (II) 0.3608; cc. 0.1 *N* $AgNO_3$. (I) 30.87, (II) 21.22.
Calc. for $C_9H_3O_3NI_4$: I, 74.58%. Found: (I) 73.21, (II) 74.65.

Ethyl Ether.—The ethyl ether was made similarly. A yield of 60%

[1] See Pratt and Miller, THIS JOURNAL, 40, 407 (1918).

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theoretical was obtained as lemon yellow needles without melting point. No other form was observed.

Subst. (I) 0.3176, (II) 0.3782; cc. 0.1 *N* $AgNO_3$. (I) 18.30, (II) 21.83.
Calc. for $C_{10}H_8O_3NI_4$: I, 73.06%. Found: (I) 73.13, (II) 73.26.

Normal Propyl Ether.—5 g. of silver salt, 8 cc. normal propyl bromide and 30 cc. ether were placed in a small pressure flask and heated to 100° for 4 hours, during which time the color gradually changed to a dirty yellow. The mixture was filtered off and extracted with 500 cc. boiling acetic acid. Yield, 4 g. or 90% theoretical. The ether was obtained as lemon yellow needles without melting point. It decomposed readily on heating.

Subst. (I) 0.2269, (II) 0.2098; cc. 0.1 *N* $AgNO_3$. (I) 12.83, (II) 11.83.
Calc. for $C_{11}H_7O_3NI_4$: I, 71.62%. Found: (I) 71.77, (II) 71.57.

Isopropyl Ether.—This was prepared similarly to the above in 82% yield. The ether gave yellow needles which did not melt.

Subst. (I) 0.1828, (II) 0.0889, cc. 0.1 *N* $AgNO_3$. (I) 10.33, (II) 5.02.
Calc. for $C_{11}H_7O_3NI_4$: I, 71.62%. Found: (I) 71.72, (II) 71.66.

Normal Butyl Ether.—Silver salt suspended in ether reacted readily with normal butyl iodide at room temperature to give a 90% yield of the ether in the form of light yellow needles without melting point.

Subst. (I) 0.3394, (II) 0.2919; cc. 0.1 *N* $AgNO_3$. (I) 18.63, (II) 16.23.
Calc. for $C_{12}H_9O_3NI_4$: I, 70.24%. Found: (I) 69.67, (II) 70.42.

Isoamyl Ether.—The isoamyl ether decomposed more readily than the preceding derivatives. It was obtained from silver salt suspended in ether and isoamyl iodide, at room temperature for 20 hours. The ether was extracted from the residue by acetic acid as yellow needles without melting point. Yield, 75%.

Subst. (I) 0.1743, (II) 0.1063; cc. 0.1 *N* $AgNO_3$. (I) 9.50, (II) 5.78.
Calc. for $C_{13}H_{11}O_3NI_4$: I, 68.90%. Found, (I) 69.18, (II) 69.01.

Normal Octyl Ether.—This was made from silver salt and normal octyl iodide in the usual way. It was recrystallized from acetic acid, avoiding long heating, and dried below 100°. The ether forms yellow needles which do not melt.

Subst. (I) 0.2944, (II) 0.3061; cc. 0.1 *N* $AgNO_3$. (I) 15.09, (II) 15.49.
Calc. for $C_{16}H_{17}O_3NI_4$: I, 65.03%. Found: (I) 65.05, (II) 64.23.

Allyl Ether.—The allyl ether from silver salt and allyl iodide gave light yellow crystals in 90% yield. No melting point.

Subst. (I) 0.1148, (II) 0.1328; cc. 0.1 *N* $AgNO_3$. (I) 6.47, (II) 7.51.
Calc. for $C_{11}H_5O_3NI_4$: I, 71.82%. Found: (I) 71.54, (II) 71.74.

Benzyl Ether.—10 g. silver salt and 35 cc. benzyl chloride were heated 2–3 hours on a water bath, during which the color changed to a dirty brown. The precipitate was filtered off and extracted with 2.5 liters of boiling acetic

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acid. The benzyl ether crystallized out on cooling as long, yellow needles without melting point. Yield, 65%.

Subst. (I) 0.1653, (II) 0.1832; cc. 0.1 N $AgNO_3$. (I) 8.74, (II) 9.67.
Calc. for $C_{15}H_7O_3NI_4$: I, 67.08%. Found: (I) 67.11, (II) 66.99.

Acetate.—5 g. of pure tetraiodophthaloxime were dissolved in 75 cc. acetic anhydride by heating below the boiling point for about 40 minutes. The acetate crystallized out on cooling in bright yellow needles. It was purified from ethyl acetate.

Subst. (I) 0.2043, (II) 0.1699; cc. 0.1 N $AgNO_3$. (I) 11.52, (II) 9.59.
Calc. for $C_{10}H_3O_4NI_4$: I, 71.62%. Found: (I) 71.60, (II) 71.62.

Benzoate.—8 g. of pure tetraiodophthaloxime were dissolved in 65 cc. of benzoyl chloride 135–150°, and heated at this temperature for 30 minutes. The benzoate was precipitated by adding alcohol, filtered, and washed free from ethyl benzoate. The yellow needles showed no melting point.

Subst. (I) 0.5980, (II) 0.6311; cc. 0.1 N $AgNO_3$. (I) 31.06, (II) 32.61.
Calc. for $C_{15}H_5O_4NI_4$: I, 65.86%. Found: (I) 65.92, (II) 65.59.

PITTSBURGH, PA.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF SMITH COLLEGE.]

ON THE ADDITION OF SODIUM ACETOACETIC ESTER TO THE AROMATIC MUSTARD OILS.

BY DAVID E. WORRALL.

Received November 16, 1917.

Introduction.

In the course of an investigation of the action of phenylhydrazine and hydroxylamine on thio derivatives it became necessary to prepare the monothioanilide of acetomalonic ester, $CH_3COCH(CSNHC_6H_5)COOC_2H_5$. No experimental details were found for the preparation of this ester and since few compounds of this type have been made, a short study was made of their synthesis and reactions.

Michael[1] first pointed out that thioanilides may be built up, through the sodium derivative, by the action of sodium malonic ester on the mustard oils. With phenyl mustard oil the reactions were expressed as follows:

$$CHNa(COOC_2H_5)_2 + C_6H_5NCS = CH(CSNa.NC_6H_5)(COOC_2H_5)_2$$

$$CH(CSNa.NC_6H_5)(COOC_2H_5)_2 + \text{acid} \longrightarrow CH(CSNHC_6H_5)(COOC_2H_5)_2$$

A similar reaction would be expected with any ester containing an acidic methylene group. Thus Ruheman[2] found that sodium cyanomalonic ester as well as sodium malonic ester added to phenyl mustard oil forming thioanilides. Sodium acetoacetic ester[3] also reacts with phenyl mustard oil.

[1] *J. prakt. Chem.*, [2] **35**, 450 (1887).
[2] *J. Chem. Soc.*, **93**, 621 (1908).
[3] Michael, *J. prakt. Chem.*, [2] **60**, 286 (1899).

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Discussion of Results.

It has been found that sodium acetoacetic ester reacts readily with phenyl, the three tolyl, *p*-bromo and *β*-naphthyl mustard oils. The ethyl and benzyl derivative of sodium acetoacetic ester reacts less readily with phenyl mustard oil. The additions, with the exception of the substituted esters go readily at room temperature, although to increase the speed of reaction the mixtures were usually heated in a water bath. Since the mustard oils react with alcohol to form substituted thio urethanes ether was used as a diluent. For this reason sodium ethoxide was not used to prepare sodium acetoacetic ester, although considerable trouble was experienced in the preparation by the use of metallic sodium because of unchanged metal.

The reaction between mustard oil and the sodium compound takes place as follows:

$$CH_3COCHNaCOOC_2H_5 + RNCS = CH_3COCH(CSNa.NR)COOC_2H_5$$

The attachment of sodium to sulfur was established by condensing the sodium derivative with ethyl iodide and heating the resulting oil with acid. It decomposed in such a way as to form ethyl mercaptan, which was recognized by its repulsive odor. An isomer of this substance was prepared by using the ethyl derivative of sodium acetoacetic ester with phenyl mustard oil, a reaction which confirms the above interpretation of the addition. The sodium addition product of the ester and mustard oil on neutralization with acid isomerizes, the hydrogen shifting from sulfur to nitrogen, to form a thioanilide.

$$CH_3COCH(CSNa.NC_6H_5)COOC_2H_5 + HCl \longrightarrow CH_3COCH\text{-}(CSHNC_6H_5)COOC_2H_5 \longrightarrow CH_3COCH(CSNHC_6H_5)COOC_2H_5.$$

This view is supported by the fact that these thioanilides condense readily with hydroxylamine and phenylhydrazine[1] splitting out hydrogen sulfide.

The thioanilides resulting from the action of phenyl mustard and *p*-substituted phenyl mustard oil together with the naphthyl derivative undergo acid decomposition easily and smoothly with alkali.

$$CH_3COCH(CSNHR)COOC_2H_5 + H_2O = CH_2(CSNHR)COOH + CH_3COOH + C_2H_5OH.$$

The reaction goes so readily that dilute alkali almost instantly brings about the hydrolysis. The resulting acid when heated decomposes at its melting point with evolution of carbon dioxide, changing almost quantitatively into a thioacetoanilide.

$$CH_2(CSNHR)COOH \longrightarrow CH_3CSNHR + CO_2.$$

While the introduction of substituents, both positive and negative, in phenyl mustard oil has no apparent effect on the addition of sodium

[1] These results will be published later.

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acetoacetic ester, the behavior of the resulting products is modified. Thus the introduction of a methyl group in the ortho and para position results in compounds which are unstable and even with careful treatment, ketonic hydrolysis takes place.

$$CH_3COCH(CSNHC_6H_4CH_3)COOC_2H_5 + H_2O = CH_3COCH_2CSNHC_6H_4CH_3 + CO_2 + C_2H_5OH.$$

Hence while phenyl mustard oil and its *p*-derivatives form esters which can be isolated unchanged, although they undergo acid hydrolysis on treatment with alkali, *o*- and *m*-tolyl mustard oils form compounds which decompose so readily that only the hydrolysis products can be isolated. The resulting ketones readily undergo further hydrolysis either with acid or alkali.

$$CH_3COCH_2CSNHC_6H_4CH_3 + H_2O = CH_3COOH + CH_3CSNHC_6H_4CH_3.$$

The replacement of hydrogen in the methylene group of acetoacetic ester by an alkyl substituent lessens the ease of addition to phenyl mustard oil, but the resulting compound is much more stable toward alkali and is decomposed only by prolonged treatment at high temperature. The benzyl derivative of sodium acetoacetic ester is still less reactive toward mustard oil. The compound formed however, is apparently a polymerized decomposition product of the expected ester.

Experimental.

Preparation of Materials.—The mustard oils were prepared by the well-known method[1] of condensing the corresponding amine with carbon bisulfide to form symmetrical disubstituted thioureas, which were decomposed by short heating with acid. The product in each case was distilled in steam and further purified by redistillation. Notwithstanding these precautions a small amount of crystalline material always separated out, on standing, from the liquid mustard oils. This was especially true with *o*-tolyl mustard oil which deposited crystals after three distillations, a characteristic that has been noted by other investigators.[2] The deposit from a lot of phenyl mustard oil was filtered out, washed and dried in vacuum. It melted at 152–153°, and when heated with concentrated hydrochloric acid formed phenyl mustard oil, proving the substance to be unchanged thiocarbanilide, which must have been carried over mechanically in the distillations.

The acetoacetic ester was converted into the sodium derivative by the use of granulated sodium.[3] The product always contained some unchanged metal and ester because the sodium derivative, which is not very soluble

[1] *Beilstein*, [3] 2, 388; Girard, *Ber.*, 6, 445 (1873); Weith, Landolt, *Ibid.*, 8, 719 (1876); Hofmann, *Ibid.*, 15, 986 (1882).

[2] Mainzer, *Ber.*, 16, 2017 (1883).

[3] Bruhl, *Ibid.*, 35, 3516 (1902).

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in ether, had a tendency to enclose the metallic sodium and prevent further reaction. This difficulty was not experienced with the ethyl derivative of the ester which forms a sodium compound readily soluble in ether.

Ethylacetomalonate Monothioanilide, $CH_3COCH(CSNHC_6H_5)COO-C_2H_5$.—Ten grams of acetoacetic ester were converted into the sodium derivative in 8–10 volumes of dry ether, to which were added 10.4 g. of phenyl mustard oil. The sodium compound which had largely separated out, went into solution in a few minutes and at the same time a viscid pale yellow oil began to form on the sides of the flask. This deposit later became crystalline and subsequently the new substance separated directly as a solid. Ice water was poured into the mixture after twelve hours' standing at room temperature. The aqueous layer was extracted again with ether and then added drop wise, with stirring, to cold well diluted hydrochloric acid. The heavy yellow oil which formed hardened slowly to a crystalline mass. This was washed, recrystallized from alcohol and dried in a vacuum desiccator. Yield of crude product, about 12 g.

0.2 subst. gave 9.8 cc. N_2 at 17° and 756 mm.
Calc. for $C_{13}H_{15}O_3NS$: N, 5.3. Found: N, 5.7.

Properties of Ethylacetomalonate Monothioanilide.—It is readily soluble in alcohol, benzene, acetone, ammonium hydroxide and sodium hydroxide solution. It crystallizes from alcohol in pale yellow, prismatic needles, which melt slowly at 82–83°. The thioanilide is very unstable toward alkaline reagents, more stable with the mineral acids but easily decomposed by the latter if heated. It is extremely soluble in ammonium hydroxide, from which an oil separates on standing.

Action of Hydrochloric Acid.—A small amount of the substance was heated with concentrated hydrochloric acid for a few minutes. Hydrogen sulfide was evolved and then the pleasant odor of ethyl acetate was observed. The acid solution was then evaporated to dryness and the crystalline residue identified as aniline hydrochloride. An alcoholic solution of silver nitrate on warming decomposed the thio derivative with the formation of silver sulfide. The alcohol was oxidized to acetaldehyde.

Action of Sodium Hydroxide.—Two grams of the substance were dissolved in a small volume of warm sodium hydroxide solution. The mixture was cooled and cautiously neutralized with hydrochloric acid. The bulky precipitate of brilliant yellow plates which formed was filtered and dried. The new substance melted with evolution of carbon dioxide at 91–92° and formed a white precipitate with silver nitrate which immediately blackened. The oil from the carbon dioxide evolution hardened to a solid, which was crystallized from alcohol in yellow prisms melting at 75°. These characteristics identified the first derivative as the thioanilide of malonic acid, a substance which Ruheman[1] obtained from another ester.

[1] *J. Chem. Soc.*, 93, 624 (1908).

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It is formed in this case by the acid hydrolysis of the acetomalonic ester derivative as follows:

$$CH_3COCH(CSNHC_6H_5)COOC_2H_5 + 2H_2O = CH_3COOH + C_2H_5OH + CH_2(CSNHC_6H_5)COOH$$

Thioacetoacetyl-*o*-toluide, $CH_3COCH_2CSNHC_6H_4CH_3$.—Five grams of *o*-tolyl mustard oil were added to sodium acetoacetic ester. The mixture was refluxed for several hours and the viscid oil which separated out was dissolved in cold water and acidified with the usual precautions. The heavy yellow oil which formed, crystallized in a few minutes. It was recrystallized from alcohol and dried in a vacuum desiccator. Yield of crude product, about 7 g.

0.1 g. gave 6.2 cc. N_2 at 21° and 754 mm.
Calc. for $C_{11}H_{13}ONS$: N, 6.8. Found: N, 7.0.

Attempts to obtain the acetomalonate derivative failed; instead ketone hydrolysis of the expected compound always took place.

Properties of Thioacetoacet-*o*-toluide.—It dissolves readily in the usual solvents, crystallizing from alcohol in slender, nearly colorless needles which melt slowly at 73–75°. It decomposes somewhat on long standing and the sharp characteristic odor of acetic acid is developed. It is very easily decomposed by alkali.

Action of Hydrochloric Acid.—Two grams of the toluide were heated with a few cc. of concentrated hydrochloric acid for a few minutes. It was then cooled and the crystalline mass separated from the acid. Alcohol was added to the latter and on warming the pleasant odor of ethylacetate was given off, proving acetic acid to be one of the products of the reaction. The precipitate was recrystallized several times from ligroin, finally separating as shining (nearly) colorless needles which melted at 91–92°.

0.1 g. gave 7.8 cc. N_2 at 21° and 756 mm.
Calc. for $C_9H_{11}NS$: N, 8.5. Found: N, 8.8.

The substance was readily soluble in cold alkali, from which it could be precipitated unchanged by acid. It appeared to be thioacetyl-*o*-toluide.

$$CH_3COCH_2CSNHC_6H_4CH_3 + H_2O = CH_3COOH + CH_3CSNHC_6H_4CH_3.$$

This thiotoluide was first prepared by Wallach[1] who described it as melting at 67–68°. It was also obtained by dissolving acetoacetic thiotoluide in cold alkali and neutralizing carefully with acid. The ether layer from the original preparation, on evaporation deposited several large crystals of the thioacetyl toluide, indicating the extreme sensitiveness of acetoacetyl thiotoluide toward alkali.

Thioacetoacetyl-*m*-toluide, $CH_3COCH_2CSNHC_6H_4CH_3$.—One gram of acetoacetic ester was converted into the sodium derivative and the molecular equivalent of *m*-tolyl mustard oil added. The mixture was refluxed

[1] *Ber.*, 13, 529 (1880).

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for an hour, the voluminous crystalline precipitate shaken with ice water and treated with acid in the usual manner. The yellow oil which separated out hardened to a crystalline mass, which was digested with a little ether and dried on a porous plate. It melted at 83–84°.

0.1 g. subst. gave 6.5 cc. N_2 at 22° and 754 mm.
Calc. for $C_{11}H_{13}ONS$: N, 6.8. Found: N, 7.3.

Action of Sodium Hydroxide.—The new compound was dissolved in warm sodium hydroxide solution, cooled and neutralized with acid. An oil separated out which did not harden on standing.

Ethylacetomalonate Monothio-*p*-toluide, $CH_3COCH(CSNHC_6H_4CH_3)$-$COOC_2H_5$.—Five grams of *p*-tolyl mustard oil were added to the equivalent amount of sodium acetoacetic ester and the mixture kept at room temperature overnight. A bulky, crystalline precipitate settled out. This was filtered, washed with dry ether and dried in vacuum. Most of this substance was dissolved in ice water, and added slowly to dilute acid. A yellow oil separated out which subsequently solidified. It was recrystallized and dried in a vacuum. Yield, 4–5 g.

0.2 g. subst. gave 9 cc. N_2 at 20° and 762 mm.
Calc. for $C_{14}H_{17}O_3NS$: N, 5.0. Found: N, 5.1.

Properties of Ethylacetomalonate Monothio-*p*-toluide.—It is readily soluble in alcohol, benzene, sodium hydroxide solution and ammonium hydroxide. It crystallizes from alcohol in shining, diamond-shaped tablets, which melt at 81°. The crystals are nearly colorless, although the alcohol solution is decidedly yellow.

Sodium Salt of Ethylacetomalonate Monothio-*p*-toluide, CH_3COCH-$(CSNa.NC_6H_4CH_3)COOC_2H_5$.—This derivative as prepared above, separated in small, colorless needles which melted at 61–62° with decomposition.

0.1 g. subst. formed 0.0225 g. Na_2SO_4.
Calc. for $C_{14}H_{16}O_3NSNa$: Na, 7.64. Found: Na, 7.54.

Action of Sodium Hydroxide.—Two grams of the toluide ester were dissolved in a small volume of warm sodium hydroxide solution and carefully neutralized, after cooling, with acid. The brilliant yellow crystals which immediately filled the beaker, were filtered, recrystallized from water and dried in vacuum.

0.1 g. subst. gave 6.1 cc. N_2 at 23° and 756 mm.
Calc. for $C_{10}H_{11}O_2NS$: N, 6.7. Found: N, 6.8.

The new compound was malonic acid monothio-*p*-toluide,

$$CH_2(CSNHC_6H_4CH_3)COOH.$$

Properties of Malonic Acid Monothio-*p*-toluide.—It crystallizes from hot water in long, colorless, flat needles which melt with foaming, due to the evolution of carbon dioxide, at 97°. It has a very bitter taste, a characteristic shared by the parent substance from which it is derived and

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the thiotoluide into which it is easily changed by heat. Silver nitrate and mercuric chlorides form amorphous white precipitates which darken on standing.

Action of Heat on Malonic Acid Monothio-*p*-toluide.—A small amount of the substance was heated slightly above the melting point in a glycerine bath, until the evolution of carbon dioxide was completed. The resulting oil immediately solidified on cooling and was recrystallized from alcohol in long, shining needles which melted at 129.5–130.5°.

0.1 g. subst. gave 8.0 cc. N_2 at 23° and 756 mm.
Calc. for $C_9H_{11}NS$: N, 8.5. Found: N, 8.8.

The product was thioaceto-*p*-toluide, identical with the preparation of Wallach.[1]

Ethylacetomalonate Monothio-*p*-bromoanilide, $CH_3COCHCSNHC_6H_4BrCOOC_2H_5$.—Three grams of *p*-bromophenyl mustard oil were added to the equivalent amount of sodium acetoacetic ester, suspended in ether, and kept at room temperature for twelve hours, during which time a yellowish white crystalline product formed. The mixture was shaken with water and treated with acid in the usual way. The yellow oil separating out hardened, on standing overnight in an ice chest. Yield, 4 g. The product was digested with a little ether and dried in a vacuum. It melted at 81–83°.

0.2 g. subst. gave 7.8 cc. N_2 at 23° and 758 mm.
Calc. for $C_{13}H_{14}O_3NSBr$: N, 4.1. Found: N, 4.4.

Action of Sodium Hydroxide.—Two grams of the ester were dissolved in a little warm sodium hydroxide solution, cooled and neutralized with hydrochloric acid. The precipitate was filtered, recrystallized from water and dried in vacuum.

0.2 g. subst. gave 9.4 cc. N_2 at 18° and 760 mm.
Calc. for $C_9H_8O_2NSBr$: N, 5.1. Found: N, 5.4.

Evidently malonic acid monothio-*p*-bromoanilide, $CH_2(CSNHC_6H_4Br)COOH$ was formed as a result of the hydrolysis.

Properties of Malonic Acid Monothio-*p*-bromoanilide.—It is easily soluble in alcohol, benzene, sodium and ammonium hydroxide solutions. The bromoanilide crystallizes from water in cream-colored flattened needles and plates. It is impossible to ascertain accurately the melting point, since a new substance of high melting point is formed when this derivative is heated. If heated slowly it changes imperceptibly to the new substance, but if plunged into a bath heated to 131°, it partially melts with foaming, then rehardens. The bromo derivative forms an unstable white silver salt which changes, on standing, to silver sulfide.

Thioaceto-*p*-bromoanilide, $CH_3CSNHC_6H_4Br$.—One gram of the malonic acid thiobromoanilide was heated in an oil bath to 150° for a few

[1] *Ber.*, 13, 529 (1880).

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minutes. The product was recrystallized from alcohol in colorless, six-sided, narrow plates which melted at 153°.

0.1 g. subst. gave 5.5 cc. N_2 at 20° and 764 mm.
Calc. for C_8H_8NSBr: N, 6.1. Found: N, 6.3.

Ethylacetomalonate Monothio-β-naphthylamide, $CH_3COCH(CSNHC_{10}H_7)COOC_2H_5$.—1.5 g. of β-naphthyl mustard oil were added to the corresponding amount of sodium acetoacetic ester in ether. The yellowish white precipitate which formed after twelve hours' standing was treated in the customary manner, resulting in a heavy yellow oil which did not solidify on standing. No analysis was made of the substance because of the uncertainty of the purification and the small amount available, but the behavior with alkali afforded a check on the compound so that there is little doubt that the above interpretation is correct.

Action of Sodium Hydroxide.—The oil was dissolved in warm sodium hydroxide solution and carefully neutralized with acid. The resulting voluminous precipitate was recrystallized from water in pale yellow plates and flattened needles which melted at 87–89° with foaming.

0.1 g. subst. gave 5.2 cc. N_2 at 21° and 758 mm.
Calc. for $C_{13}H_{11}O_2NS$: N, 5.7. Found: N, 5.9.

The new derivative is malonic acid monothio-β-naphthylamide, $CH_2(CSNHC_{10}H_7)COOH$. The fragment of material remaining was heated on a water bath until the evolution of carbon dioxide had ceased. The yellow oil hardened on cooling to a crystalline mass which melted at 119–122° and was an impure form of thioaceto-β-naphthylamide. This substance when pure melts at 145–146°.[1]

Ethylacetoethylmalonate Monothioanilide, $CH_3COC(C_2H_5)(CSNHC_6H_5)COOC_2H_5$.—Ten grams of the ethyl derivative of ethylacetoacetic ester were converted into the sodium derivative and 8.6 g. of phenyl mustard oil added to the clear ether solution of the ester. A compact crystalline precipitate separated out on the sides of the flask after it had been refluxed two hours. It was heated for another hour and the solid filtered, washed with dry ether and dried over calcium chloride. Most of the sodium derivative was treated with acid, observing the usual precautions and the ester separated in good yield as an oil which did not harden on standing. The sodium derivative was used for analysis.

0.3415 g. subst. gave 0.0741 Na_2SO_4.
Calc. for $C_{15}H_{18}O_3NSNa$: Na, 7.3. Found: Na, 7.1.

Properties of Ethylacetoethylmalonate Monothioanilide.—The substance is an oil which is miscible with organic solvents, also sodium or potassium hydroxide. It is much more stable toward alkali than the corresponding acetomalonate derivative and is not hydrolyzed by cold caustic

[1] Sullwald, *Ber.*, **21**, 2627 (1888).

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alkali solutions. Boiling hydrochloric acid acted slowly on the ester, but without the formation of crystalline compounds.

Action of Potassium Hydroxide.—Two grams of the ester were dissolved in a rather concentrated water solution of potassium hydroxide and refluxed for several hours, during which time an oil gradually separated out. The mixture was distilled with steam and a small amount of a colorless oil with a penetrating but not unpleasant odor came over and dissolved in the distillate. The original mixture still retained a red oil which solidified on cooling. It was filtered, washed and crystallized several times from ligroin, finally separating in colorless, shining, square plates which melted at 94–95°. The filtrate from the first separation when acidified, evolved hydrogen sulfide and a copious yellow precipitate formed. This was separated and recrystallized from water in glistening, irregular plates. The new substance when heated melted at 150–151° with foaming, due to evolution of carbon dioxide and changed to a compound which melted at 94–95°, thus proving the identity of the latter with the substance insoluble in alkali. The presence of both sulfur and nitrogen was proved in each case. The lower melting derivative was found to contain about 15% N_2. The compounds which were evidently the result of deep-seated reactions, involving not only hydrolysis, but probably oxidation, were not identified because of the limited amount of material.

Action of Sodium Benzylacetoacetic Ester on Phenyl Mustard Oil.—Five grams of benzylacetoacetic ethyl ester were converted into the sodium derivative in ether and treated with 3.06 g. of the mustard oil. The mixture was refluxed for twelve hours without any change, so the ether was evaporated off and replaced with toluene. Two hours' boiling with the latter resulted in the formation of a yellow crystalline mass which was separated, dissolved in ice water and extracted with ether. The cold solution was then added dropwise, with stirring, to hydrochloric acid well diluted and cooled with ice. A bulky, yellow precipitate formed which immediately changed and coagulated to an orange-colored pasty, ball, which was separated, digested with warm alcohol and filtered while warm. The residue was washed well with cold alcohol and dried in an oven at 100°. The yield of purified product was very poor.

0.2 g. subst. gave 10.4 cc. N_2 at 17° and 760 mm.
Calc. for $(C_{15}H_{16}NS)_x$: N, 5.8. Found: N, 6.0.

The new substance as prepared consisted of microscopic flattened bars, yellow in color. It is nearly insoluble in alcohol, benzene, sodium hydroxide solution and hydrochloric acid. It melts at 222–223° with decomposition. The inert character of the substance, especially toward alkali, and its high melting point indicated the formation of a polymer; hence it was called bis-benzylthioacetanilide, $CH_2(CSNHC_6H_5)CH_2C_6H_5$, although the molecular weight was not determined or the structure.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

OXALYL CHLORIDE AS A REAGENT IN ORGANIC CHEMISTRY. II. PREPARATION OF AROMATIC ACID ANHYDRIDES; REACTION WITH ALCOHOLS.

BY ROGER ADAMS, W. V. WIRTH AND H. E. FRENCH.

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In a previous paper[1] the action of oxalyl chloride on phenols in the presence of pyridine and at a very low temperature was shown to give practically quantitative yields of the corresponding oxalic acid esters. This reaction is of particular value in the identification of phenols. During that investigation it was found that oxalyl chloride often had a decided tendency to act as a dehydrating agent and consequently its action[2] on primary, secondary and tertiary alcohols was also studied to see whether it might give a general way of preparing olefines from alcohols. A continuation of the study of oxalyl chloride is described in this paper, the first part dealing with its use as a dehydrating agent to form anhydrides from aromatic acids and the second part with its value as a reagent for the identification of alcohols just as it was for phenols.

Preparation of Aromatic Acid Anhydrides.

When one molecule of oxalyl chloride was allowed to stand with one molecule of benzoic acid for several days, the benzoic acid gradually disappeared, though not completely, and at the same time gases were evolved. On distillation, it was found that the reaction product consisted of benzoyl chloride and a small amount of unchanged benzoic acid. The reaction undoubtedly took place according to the following equation:

$$C_6H_5COOH + (COCl)_2 = C_6H_5COCl + CO + HCl + CO_2$$

In an attempt to hasten the speed of the reaction, a similar mixture of oxalyl chloride and benzoic acid was refluxed for about two hours. On distillation of the product, however, the yield of benzoyl chloride was much smaller than when the reaction ran in the cold and a large amount of another product boiling at 360°, which proved to be benzoic anhydride, formed at the same time. A thorough study was made of the action of oxalyl chloride on aromatic acids with and without various solvents, until ideal conditions were found for producing the corresponding acid anhydrides. Thus when slightly over one molecule of oxalyl chloride was added to a boiling solution or suspension in benzene of two molecules of an aromatic acid, the best results were obtained, and upon evaporation of the benzene very good yields of anhydrides resulted. These anhydrides contained only a small by-product of unchanged acid, which was readily removed with a sodium carbonate solution, and practically no

[1] THIS JOURNAL, 37, 2716 (1915).

[2] *Ibid.*, 38, 2514 (1916).

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by-product of acid chloride. The equation for the above reaction may be represented as follows:

$$2C_6H_5COOH + (COCl)_2 = (C_6H_5CO)_2O + 2HCl + CO + CO_2$$

It seemed probable, however, from a study of certain of the substituted benzoic acids, that the mechanism was not as simple as represented by the above equation, but that two steps were involved, the formation of the mixed anhydride of oxalic acid and the aromatic acid, then decomposition of this to the acid anhydride desired.

$$2C_6H_5COOH + (COCl)_2 = (C_6H_5COOCO)_2 + 2HCl.$$

$$(C_6H_5COOCO)_2 = (C_6H_5CO)_2O + CO + CO_2.$$

The evidence for this mechanism resulted from the isolation of a few of the mixed anhydrides when oxalyl chloride reacted with certain substituted benzoic acids. The *m*-nitrobenzoic acid, the 2,4- and 3,5-dinitrobenzoic acids all formed crystalline mixed anhydrides, which separated out from the benzene during the course of the reaction. These substances were stable to sodium carbonate solution but decomposed quantitatively upon melting to give carbon monoxide, carbon dioxide and the simple acid anhydride. Cold pyridine in the same way effected immediate decomposition of the mixed anhydrides with the evolution of carbon monoxide and carbon dioxide. It was probable, therefore, that in every case these substances were formed primarily, but with many of the acids they were unstable under the conditions of the reaction and broke down into the simple acid anhydrides. The formation of these mixed anhydrides was not dependent upon the presence of a nitro group, for the *o*-nitrobenzoic acid gave the *o*-nitrobenzoic anhydride in one step in the usual way. The relative insolubility of these particular mixed anhydrides in benzene undoubtedly favored their isolation before decomposition had a chance to take place.

The disadvantages of the general methods available at the present time for the preparation of aromatic acid anhydrides and the advantage of the new method described here may be seen at once. Many of the methods described in the literature make use of the aromatic acid or the salt of the aromatic acid with such reagents as phosphorus oxychloride, sulfur chloride, or phosphorus pentachloride. The fact that such strong reagents as those just mentioned must be used, limits the reactions to the preparation of those aromatic acid anhydrides which contain no easily attacked substituting group in the benzene nucleus. Moreover, a by-product of acid chloride, often not easily removed, is invariably obtained. Other methods make use of the aromatic acid chloride in condensation with a large variety of different reagents. Practically none of these processes gives very good yields and most of them give rise to by-products which are none too easily removed. In addition, it may be pointed out

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that the aromatic acid chlorides themselves are often quite troublesome to prepare. Another method generally mentioned in text-books for the synthesis of aromatic acid anhydrides is to treat the aromatic acid with acetic anhydride. This process seldom gives over 50% yields and often much smaller ones, and as by-products mixed anhydrides of acetic acid and the aromatic acid always form. The method described in this paper is extremely simple, using a reagent most readily obtainable. The yields are very good and no side products form to interfere with the purification of the product. It may, therefore, be recommended as the best and quickest way of securing aromatic acid anhydrides in a pure state.

Experimental Part.

The general process to be followed for the preparation of the anhydrides is as follows: Suspend 5 g. of powdered aromatic acid in about 20 cc. of dry benzene and place in a round-bottom flask attached to a reflux condenser. (It is preferable but not absolutely necessary to have the flask ground to the inside tube of the condenser as oxalyl chloride has a tendency to attack cork stoppers.) Heat the mixture to gentle boiling and allow 1.2 molecules of oxalyl chloride to drop in slowly through the condenser. Each drop causes an immediate evolution of gas and this continues for some time after all the oxalyl chloride has been added. Continue the refluxing for one or two hours to be sure that the reaction is complete. Evaporate off the benzene and wash the solid residue with sodium carbonate solution to take out any small amount of unchanged acid. The product remaining is the acid anhydride and for ordinary work does not need further purification. The yields of the anhydride vary from 70 to 85% of the theory calculated on the amount of acid used, but since some acid is recovered in every case, the yields are actually better than those just mentioned. In working with acids which were very insoluble in benzene, it is advisable to use a slightly larger amount of oxalyl chloride and to reflux the mixture a longer time. Wherever a mixed anhydride forms, the procedure is just the same. It involves an extra step, however, the melting of the reaction product after it has been washed with sodium carbonate solution and dried. The pure anhydride is thus obtained.

By the above procedure, 13 aromatic anhydrides were prepared, some of which had already been made by other methods and some of which had not been synthesized until this time. The following table gives a list of these anhydrides with their melting points.

The benzoic anhydride, the 3 toluic anhydrides, the *p*-chlorobenzoic anhydride, the *o*- and *p*-nitrobenzoic anhydrides and anisic anhydride were all crystallized from the solvents already mentioned in the literature and gave the same crystalline forms which were published. The

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melting points in one or two cases were slightly different and are shown in the table.

TABLE I.

		This research. Melting point.	In literature. Melting point.	
1	Benzoic anhydride	42°	42°	*Ann.*, **87**, 73 (1853).
2	*o*-Toluic anhydride	36–37°	36–37°	*Ibid.*, **239**, 74 (1887).
3	*m*-Toluic anhydride	70°	71°	*J. Chem. Soc.*, **95**, 1240 (1909).
4	*p*-Toluic anhydride	94°	95°	*Ibid.*, **75**, 344 (1899).
5	*o*-Chlorobenzoic anhydride	78–79°	...	.....
6	*m*-Chlorobenzoic anhydride	95°	...	.....
7	*p*-Chlorobenzoic anhydride	193–4°	193–4°	*Ber.*, **43**, 2229 (1910).
8	*o*-Nitrobenzoic anhydride	135°	135°	*Ibid.*, **17**, 2789 (1884).
9	*m*-Nitrobenzoic anhydride	162°	...	.....
10	*m*-Iodobenzoic anhydride	134°	...	.....
11	Anisic anhydride	99°	95–6°	*Ann.*, **102**, 284 (1856).
12	3,5-Dinitrobenzoic anhydride	209°	...	.....
13	2,4-Dinitrobenzoic anhydride	160°	...	.....

***o*-Chlorobenzoic Anhydride,** $(ClC_6H_4CO)_2O$.—Small, white prismatic needles from alcohol, melting at 78–79°.

0.2346 g. subst.; 0.1161 g. AgCl.
Calc. for $C_{14}H_8O_3Cl_2$: Cl, 24.04. Found: Cl, 23.85.

***m*-Chlorobenzoic Anhydride,** $(ClC_6H_4CO)_2O$.—Short, white needles from alcohol melting at 95°.

0.2160 g. subst.; 0.2076 AgCl.
Calc. for $C_{14}H_8O_3Cl_2$: Cl, 24.04. Found: Cl, 23.99.

***m*-Iodobenzoic Anhydride,** $(IC_6H_4CO)_2O$.—White plates from alcohol melting at 134°.

0.1923 g. subst.; 0.1883 g. AgI.
Calc. for $C_{14}H_8O_3I_2$: I, 53.12. Found: I, 52.91.

***m*-Nitrobenzoicoxalic Anhydride,** $(NO_2C_6H_4COOCO)_2$.—Yellowish crystals decomposing at 157°. Only very slightly soluble in the common organic solvents. For analysis it was washed with dilute sodium carbonate solution, then dried and finally washed several times with hot benzene.

0.1906 g. subst.; 0.2788 g. CO_2; 0.0706 g. H_2O.
0.2419 g. subst.; 19.65 cc. N, 747 mm., 23.0°.
Calc. for $C_{14}H_8O_{10}N_2$: C, 49.5; H, 2.06; N, 7.2. Found: C, 49.30; H, 2.26; N, 7.5.

Upon melting this mixed anhydride, one molecule of carbon monoxide, one molecule of carbon dioxide, and one molecule of *m*-nitrobenzoic anhydride were produced. To show that this decomposition was quantitative, three g. of pure mixed anhydride were placed in a test tube connected with a potash absorption bulb and a tube through which pure air could be forced. The test tube was then heated to 170° and air passed through to sweep the carbon dioxide and carbon monoxide into the absorption

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bulb. The increase in weight due to the carbon dioxide and the loss in the weight of the mixed anhydride were recorded.

Wt. subst. before heating	3.000 g.
Wt. subst. after heating	2.409 g.
Wt. CO_2 + CO evolved	0.591 g.
Wt. CO_2 collected	0.335 g.

Calc. % loss of CO and CO_2, 19.54. Found: 19.71.
Calc. % of CO_2 evolved, 11.34. Found: 11.16.

***m*-Nitrobenzoic Anhydride,** $(NO_2C_6H_4CO)_2O$, prepared by the decomposition of the mixed anhydride of oxalic acid and *m*-nitrobenzoic acid. White crystals from benzene melting at 163°.

0.1840 g. subst.; 0.3782 g. CO_2; 0.0296 g. H_2O.
0.2675 g. subst.; 20.54 cc. N, 745 mm., 22.0°.
Calc. for $C_{14}H_8O_7N_2$: C, 53.16; H, 2.54; N, 8.86. Found: C, 53.03; H, 2.78; N, 9.50.

m-Nitrobenzoic anhydride was described in the literature by Autenrieth,[1] who made it by the action of acetic anhydride on *m*-nitrobenzoic acid and reported the melting point as 47°. His work was repeated in this laboratory and it was found that provided the reaction was carried out as described, a substance melting at 47° was actually obtained. If, however, the reaction mixture was heated longer and the temperature raised to 175° after the excess of acetic anhydride was distilled off, a good yield of the *m*-nitrobenzoic anhydride melting at 162° resulted. The substance melting at 47° was undoubtedly the mixed anhydride of acetic acid and *m*-nitrobenzoic acid described by Green,[2] who reported the melting point at 45°. This mixed anhydride on high heating decomposed into the *m*-nitrobenzoic anhydride.

3,5-Dinitrobenzoicoxalic Anhydride, $[(NO_2)_2C_6H_3COOCO]_2$, slightly yellowish crystalline powder decomposing at 175°.

0.1625 g. subst.; 0.2382 g. CO_2; 0.0112 g. H_2O.
0.2400 g. subst.; 25.56 cc. N, 741 mm., 23.0°.
Calc. for $C_{16}H_6O_{14}N_4$: C, 40.16; H, 1.25; N, 11.7. Found: C, 39.89; H, 1.41; N, 12.0.

3,5-Dinitrobenzoic Anhydride, $[(NO_2)_2C_6H_3CO]_2O$, short, white crystals from benzene melting at 109°.

0.3319 g. subst.; 23.96 cc. N, 740 mm., 22.0°.
Calc. for $C_{16}H_6O_{11}N_4$: N, 13.79. Found: 14.05.

2,4-Dinitrobenzoicoxalic Anhydride, $[(NO_2)_2C_6H_3COOCO]_2$, slightly yellowish crystalline powder melting with decomposition at 205–209°. This substance was not analyzed but was decomposed directly into the simple anhydride.

2,4-Dintrobenzoic Anhydride, $[(NO_2)_2C_6H_3CO]_2O$, white crystalline powder from benzene, melting at 160°.

[1] *Ber.*, **34**, 184 (1901).
[2] *Ann.*, **11**, 415 (1889).

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0.2485 g. subst.; 25.9 cc. N, 740 mm., 22.0°.
Calc. for $C_{14}H_6O_{11}N_4$: N, 13.8. Found: 13.1.

Oxalyl Chloride in the Presence of Pyridine with Secondary and Tertiary Alcohols.

Oxalyl chloride[1] reacted instantaneously with primary alcohols to give the corresponding oxalic acid esters. With secondary alcohols, however, either olefines or ethers resulted and with tertiary alcohols, chlorides formed in most cases. It seemed possible that since phenols reacted so readily and quantitatively with oxalyl chloride in the presence of pyridine to give well crystallized oxalic acid esters that oxalyl chloride with pyridine might also give esters of oxalic acid with the various kinds of alcohols and thus might prove to be a convenient way of identifying alcohols in general. As the oxalyl chloride alone reacted in the cold to give quantitative yields of esters with the primary alcohols, this investigation was limited to the study of secondary and tertiary alcohols. The results showed that the secondary alcohols under the above-mentioned conditions gave esters of oxalic acid. Thus benzhydrol, phenyltolylcarbinol, menthol, borneol, benzoin, piperonyolin, iso-propylalcohol, etc., gave the expected derivatives, although with oxalyl chloride alone,[1] no ester formed. The yields averaged about 50%.

The tertiary alcohols with oxalyl chloride and pyridine did not give satisfactory results. The amounts of the products were very small when any ester at all was produced, the tertiary alcohols being recovered unchanged in most cases.

It is evident, therefore, that oxalyl chloride in the presence of pyridine has the same disadvantages as the other alcohol reagents, such as acetyl chloride, benzoyl chloride, phenyl isocyanate, diphenyl chlorourea, etc., in that it does not react satisfactorily with tertiary alcohols. With secondary alcohols, however, it may be recommended; as the reaction can be carried out at low temperatures and the compounds in most cases are well crystallized and easily purified solids. Many other alcohol reagents react with much more difficulty with secondary alcohols than the one mentioned above and the reaction products are often liquids, whereas solids were obtained in this research.

Experimental Part.

The general procedure in this investigation was as follows: Cool 25 cc. of pyridine with ice and add one molecule of oxalyl chloride, drop by drop. A yellow addition product separates out immediately and must be crushed with a spatula. Add to this mixture two molecules of the alcohol dissolved in a little pyridine; allow the mixture to stand two or more hours either in a freezing mixture or at room temperature, then pour into ice and hydrochloric acid. The pyridine goes into solution and the

[1] THIS JOURNAL, 38, 2514 (1916).

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ester separates out and may be filtered off or separated if it happens to be a liquid.

Benzhydrol Oxalate, $[(C_6H_5)_2CH]_2C_2O_4$, made at 0°. Small white needles from petroleum ether melting at 142–143°.

0.1841 g. subst.; 0.5386 g. CO_2; 0.0906 g. H_2O.
Calc. for $C_{28}H_{22}O_4$: C, 79.62; H, 5.21. Found: C, 79.76; H, 5.46.

Phenyl-tolyl-carbinol Oxalate, $[C_6H_5(CH_3C_6H_4)CH]_2C_2O_4$, made at 0°. White crystals from ligroin melting at 86–87°.

0.1916 g. subst.; 0.5596 g. CO_2; 0.1029 g. H_2O.
Calc. for $C_{30}H_{26}O_4$: C, 80.00; H, 5.77. Found: C, 79.64; H, 5.96.

An attempt was made to prepare phenyl-anisyl carbinol from phenyl-anisyl ketone and sodium amalgam. The carbinol was obtained, but only in small yields, and so was not used in subsequent work. The melting point is considerably higher than 58°, which is reported in the literature.[1] An alcohol solution of 25 g. of phenyl-anisyl ketone was treated with 1 kg. of sodium amalgam. This was allowed to stand overnight, then refluxed on a water bath for two hours. Upon distilling the alcohol, adding water and dilute sulfuric acid to acidify, and finally extracting with ether, a substance was obtained in the ether which crystallized from ligroin in white needles melting at 68° and on analysis proved to be phenyl-anisyl carbinol.

0.2000 g. subst.; 0.5761 g. CO_2; 0.1184 g. H_2O.
Calc. for $C_{14}H_{14}O_2$: C, 78.50; H, 6.54. Found: C, 78.55; H, 6.57.

Dibenzoin Oxalate, $[C_6H_5CO(C_6H_5)CH]_2C_2O_4$, made at room temperature. Fine, white crystals from nitrobenzene, melting at 243–245°.

0.1992 g. subst.; 0.5454 g. CO_2; 0.0852 g. H_2O.
Calc. for $C_{30}H_{22}O_6$: C, 75.31; H, 4.60. Found: C, 74.67; H, 4.75.

Dipiperonyloin Oxalate, $[CH_2O_2C_6H_3CO(CH_2O_2C_6H_3)CH]_2C_2O_4$, made at room temperature. White powder from nitrobenzene melting at 225–226°.

0.2203 g. subst.; 0.4983 g. CO_2; 0.0728 g. H_2O.
Calc. for $C_{34}H_{26}O_8$: C, 62.39; H, 3.36. Found: C, 61.68; H, 3.67.

Borneol Oxalate, $(C_{10}H_{17})_2C_2O_4$, made at room temperature. White crystals from alcohol melting at 108–109°. From oxalic acid and borneol[2] the oxalate is reported as melting at 113°.

0.1898 g. subst.; 0.5091 g. CO_2; 0.1666 g. H_2O.
Calc. for $C_{22}H_{34}O_4$: C, 72.92; H, 9.39. Found: C, 73.15; H, 9.75.

Menthol Oxalate, $(C_{10}H_{19})_2C_2O_4$, white crystals from benzol, melting at 66–67°. Same melting point obtained as when it was prepared from oxalic acid[3] and menthol.

[1] *J. prakt. Chem.*, [2] **77**, 20 (1908).
[2] C., [1] 998 (1908): D. R. P. 193,301.
[3] *Ber.*, **35**, 2474 (1902).

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Isopropyl Oxalate, $[(CH_3)_2CH]_2C_2O_4$, colorless liquid boiling at 189°. Boiling point[1] previously reported is 190°.

Tertiary Alcohols.

Triphenyl carbinol, diethyl-phenyl carbinol and diphenyl-methyl carbinol were studied. In the first two cases no oxalates were obtained, the alcohols being recovered. With the third, however, a small yield of the oxalic acid ester was produced. This was separated from the unchanged carbinol by treatment with cold benzene in which it did not dissolve, then crystallized from hot benzene in colorless pyramids softening at 110° and decomposing gradually between 170–185° with the evolution of gas.

0.2056 g. subst.; 0.6043 g. CO_2; 0.1119 g. H_2O.
Calc. for $C_{30}H_{26}O_4$: C, 80.0; H, 5.77. Found: C, 80.14; H, 6.04.

[Contribution from the Division of Agricultural Biochemistry, Minnesota Agricultural Experiment Station.]

THE PRESERVATION OF PLANT JUICES FOR ANALYSIS OF SUGAR CONTENT.[2]

By D. O. Spriestersbach.

Received December 12, 1917.

It is desirable at times to preserve samples for future analysis. This was the case recently at the Minnesota Experiment Station while sorghum investigations were in progress; however, certain difficulties are immediately met with when the samples consist of plant juices, *i. e.*, the extreme ease with which sugars are destroyed by microörganisms and the fact that the common disaccharides are rather easily hydrolyzed. The first difficulty can of course be overcome by the use of preservatives which either by virtue of their toxicity can kill microörganisms or are able to inhibit their growth. The second must be overcome by a means which counteracts the hydrolyzing agent, in this case principally acids. At the same time the substances employed must not in any way interfere with the proper determination of the composition of a juice. It is obvious that relatively few of the usual preserving agents meet the above conditions.

Accordingly, at the suggestion of Prof. R. M. West, a few common preservatives were tried in a preliminary way upon sorghum juice. Most of them immediately showed themselves to be unsatisfactory, the exceptions being mercuric iodide dissolved in potassium iodide solution, phenol, and toluene. The former was chosen on account of its high toxicity to microörganisms, and toluene was selected rather than phenol since it appeared to be equally efficient at the same time and was free of certain

[1] *Ann.*, 139, 229 (1866).

[2] Published with the approval of the Director as Paper No. 95, Journal Series, Minnesota Agricultural Experiment Station.

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minor disadvantages of phenol during the determination of the sugar content.

Toluene was always added in sufficient quantity to saturate the juice and to leave an excess of a few cubic centimeters to gather in droplets at the surface. The mercuric iodide was at first made up in solution in such quantity that the required amount could be added with a pipet when collecting samples in the field. Table I shows the effect of this dilution in the two last samples. The errors introduced by this dilution were so

TABLE I.—SHOWING THE PRESERVATIVE ACTION OF MERCURIC POTASSIUM IODIDE AND TOLUENE UPON SORGHUM JUICE.

No.	Preservative.	Date analyzed.	Per cent. sucrose.	Per cent. reducing sugar.[1] R.	Per cent. reducing sugar[1] after inversion. R'.	R'—R.
3173	None	10/17/14	8.9	4.8	13.4	8.6
		22	3.1	7.6	10.4	2.8
		27	0.4	7.7	7.6	....
3179	Toluene	10/17/14	9.0	4.8	13.5	8.7
		22	7.2	6.9	14.0	7.1
		27	4.6	9.2	13.8	4.6
		11/ 4/14	2.2	11.6	13.7	2.1
		13	0.4	13.2	13.2	....
		6/ 7/15	....	13.5	13.6	0.1
3180	0.05% mercuric potassium iodide	10/17/14	10.1	3.7	13.5	9.8
		22	9.7	4.2	13.8	9.6
		27	9.1	4.5	13.9	9.4
		11/ 4/14	8.7	5.0	13.9	8.9
		13	8.2	5.6	13.7	8.1
		6/ 7/15	....	12.0	13.7	1.7
3181	0.05% mercuric potassium iodide plus 1.8 grams sodium carbonate	10/17/14	10.6	3.1	13.3	10.2
		22	10.5	3.5	13.7	10.2
		27	10.0	3.5	13.7	10.2
		11/ 4/14	10.0	3.7	13.7	10.0
		13	9.7	3.9	13.6	9.7
		6/ 7/15	....	6.5	13.4	6.9
3182	0.1% mercuric potassium iodide	10/17/14	10.3	3.3	13.1	9.8
		22	10.0	3.9	13.7	9.8
		27	9.4	4.1	13.7	9.6
		11/ 4/14	9.1	4.6	13.7	9.1
		13	8.4	5.2	13.6	8.4
		6/ 7/15	....	12.0	13.7	1.7
3183	0.5% mercuric potassium iodide	10/17/14	10.0	3.0	12.7	9.7
		22	9.8	3.4	13.3	9.9
		27	9.2	3.7	13.0	9.3
		11/ 4/14	9.0	4.1	13.0	8.9
		13	8.5	4.5	12.9	8.4
		6/ 7/15	....	11.0	12.9	1.9

[1] Calculated as glucose.

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great that in subsequent experiments the equivalent amount of mercuric chloride required was suspended in one or two cc. of water on a watch-glass, and crystals of potassium iodide added as needed to the point of just dissolving the last trace of mercuric iodide. The resulting small amount of solution was added to the juice, and rinsed down with it, so that the error due to a volume change was negligible. The samples were all kept at room temperature in stoppered bottles.

The results of the first series of analyses are shown in Table I. No initial analysis could be made upon the sample of juice as a whole, because it was taken at an out-of-town sorghum mill two days before reaching the laboratory but the first analysis of Sample No. 3181 may be taken for reference as the original composition. The preservatives were added as shown, and on comparison it was discovered that the sample containing both mercuric potassium iodide and sodium carbonate was the best preserved. The total sugar (calculated as dextrose) remains very constant for over 6 months, while the sucrose shows only a slight inversion. This demonstrates the possibility of inhibiting the growth, as well as the killing of microörganisms which attack sugars, by means of preservatives. The control sample rapidly deteriorated, as was to be expected, due chiefly to the action of various yeasts and acid-forming bacteria.

TABLE II.—SHOWING THE PRESERVATIVE ACTION OF TOLUENE AND MERCURIC POTASSIUM IODIDE UPON AN ALKALINE SOLUTION OF DILUTED SORGHUM SIRUP.

Sample No.	Description.	Date analyzed.	Per cent. sucrose.	Per cent. glucose.
A	Diluted sirups made slightly alkaline with sodium carbonate	6/15/15	8.6	4.3
		19	8.4	4.4
		26	8.4	4.2
		7/ 3/15	8.2	4.0
		10	Slimy	...
B	Same plus toluene	6/19/15	8.4	4.4
		26	8.4	4.4
		7/ 3/15	8.5	4.3
		10	8.5	4.4
		17	8.7	4.4
		9/20/15	8.5	4.3
C	Same plus 1 g. mercuric potassium iodide per l.	6/19/15	8.4	4.5
		26	8.3	4.4
		7/ 3/15	8.5	4.3
		10	8.5	4.3
		17	8.6	4.3
		9/20/15	Slimy	...

These results being so promising, it seemed advisable to repeat and confirm them. Inasmuch as the sorghum season was over so that no natural juice could be obtained, some sirups were diluted with water and treated as a juice. In this material a different bacterial flora was present prob-

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TABLE III.—SHOWING THE PRESERVATIVE ACTION OF TOLUENE, MERCURIC POTASSIUM IODIDE AND MERCURIC NITRATE UPON BOILED AND UNBOILED SORGHUM JUICE MADE ALKALINE WITH SODIUM CARBONATE.[1]

Sample No.	Description.	Date analyzed.	Per cent. sucrose.	Per cent. glucose. R.	Per cent. reducing sugar[2] after inversion. R'.	Per cent. R' — R.
O	Original juice	10/13/16	11.8	5.8	17.9	12.1
A	2 g. sodium carbonate and 5 cc. toluene added	20	11.8	5.8	17.9	12.1
		31	11.3	5.6	19.1	13.5
		11/29/16	11.2	5.6	17.6	12.0
		1/ 2/17	6.2	10.6	15.3	4.7
O	Original juice	10/13/16	11.8	5.8	17.9	12.1
C	Boiled, cooled, made to volume and 2 g. of sodium carbonate plus 5 cc. toluene added	20	12.0	5.4	18.7	13.3
		31	11.7	5.4	18.7	13.3
		11/29/16	11.5	5.2	17.6	12.4
		1/ 2/17	5.8	10.7	16.0	5.3
O	Original juice	10/13/16	11.8	5.8	17.9	12.1
B	2 g. of sodium carbonate plus 0.1% mercuric potassium iodide added	20	11.9	5.8	17.9	12.1
		31	11.7	6.3	18.3	12.0
		11/29/16	8.2	8.6	22.2[3]	13.6
		1/ 2/17	6.0	9.8	16.0	4.2
O	Original juice	10/13/16	11.8	5.8	17.9	12.1
D	Boiled, cooled, made to volume and 2 g. of sodium carbonate plus 0.1% mercuric potassium iodide added	20	12.0	5.4	18.3	12.9
		31	11.4	5.2	17.9	12.7
		11/29/16	11.2	5.0	18.7	13.7
		1/ 2/17	10.0	6.0	13.8	7.8
O	Original juice	10/13/16	11.8	5.8	17.9	12.1
E	1 g. of sodium carbonate added, kept cool, and 2% mercuric nitrate added on the fourth day thereafter	20	10.2	6.1	17.2	11.1
		31	10.2	6.0	17.2	11.2
		11/29/16	9.4	5.0	16.4	11.4
		1/ 2/17	9.4	6.2	15.3	9.1
O	Original juice	10/13/16	11.8	5.8	17.9	12.1
F	Boiled, cooled, 1 g. sodium carbonate added, made to volume, and kept cool; 2% mercuric nitrate added on fourth day thereafter	20	12.0	5.4	17.9	12.5
		31	11.6	5.3	17.9	12.6
		11/29/16	11.3	5.3	17.2	11.9
		1/ 2/17	11.2	5.3	14.9	9.6

[1] Analyzed by A. J. Wuertz, Graduate Assistant.
[2] Calculated as glucose.
[3] Obviously erroneous.

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ably consisting largely of those organisms possessing capsules and which in some manner are able to resist boiling for a time. The results are shown in Table II.

Little inversion took place in the control sample due to the presence of sodium carbonate and the type of bacteria present. The total sugar remains very constant in the preserved samples. The fact that sucrose was apparently formed in small amounts, probably is due to errors in the methods of analysis. No further analyses could be made after the samples became slimy for they could not be filtered after adding the clarifying solution. Both preservatives were apparently equally good.

When sorghum juice was again available, another series of analyses was made. The results are shown in Table III. From these results mercuric potassium iodide apparently possesses greater preserving power than toluene, due probably to its greater toxicity and non-volatility. It has been noticed, however, that the mercury gradually becomes reduced and precipitates out, thereby decreasing its efficiency. The boiled solutions have as a rule shown themselves to be most easily preserved.

Some preliminary tests have indicated that mercuric nitrate may be even more effective as a preservative than is mercuric potassium iodide. The results of one series of analyses only are given in Table III. This shows that mercuric nitrate is a good preservative, especially in alkaline solution; moreover, it was added on the fourth day since the beginning of the series, the samples meanwhile being kept in the refrigerator. It is necessary to add larger quantities of the mercuric nitrate than of the mercuric potassium iodide since it causes a heavy precipitation which does not appear on the addition of mercuric potassium iodide. Further investigations of the value of mercuric nitrate as a preservative are desirable.

Summary.

The preservation of sweet juices for subsequent analysis presents two great difficulties, the prevention of (1) fermentation, and (2) hydrolysis. The preservative action of toluene and mercuric potassium iodide has been accordingly tested. The latter seems to possess the greater preserving action, and both show maximum effect in boiled samples which have been rendered slightly alkaline. The recommended procedure is to take a sample of definite volume, neutralize with a slight excess of calcium carbonate, boil for a few minutes, add 2 grams of anhydrous sodium carbonate per liter of juice, then add the preservative, cool to the original temperature, make up to the original volume taken and shake well. A too great excess of sodium carbonate destroys some of the reducing sugar. The density of the original juice may be taken with a Brix hydrometer, and the sample of preserved juice taken for analysis with a sucrose pipet to the original Brix value. In this way, the weight of the original juice is known as a basis for calculation, and the sugar content of the sample of

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preserved juice will be the same as the original at the same temperature.

Preliminary experiments and one series of analyses indicate that mercuric nitrate may possess greater preserving action than mercuric potassium iodide.

St. Paul, Minn.

[Contribution from the Chemical Research Laboratory, The Upjohn Company.]

AN EXAMINATION OF THE LEAVES OF ADONIS VERNALIS.

By Frederick W. Heyl, Merrill C. Hart and James M. Schmidt.

Received November 14, 1917.

Adonis vernalis L. is an anemonaceous plant of the family *Ranunculaceae*. It grows natively in Central Europe and in Asia, where it is known as the Bird's eye, Pheasant's eye or False Hellebore.

Extracts of the drug were first introduced into medicine in 1879 by Bubnow,[1] who employed them as a cardiac stimulant. Cervello,[2] interested by the favorable report of Bubnow, described a method for the preparation of an active digitalis like glucoside from *Adonis vernalis*, following the method employed in the manufacture of "Digitalin German" from Digitalis seeds. The plant was macerated for two days with 50% alcohol, and the extract after filtration was precipitated with lead subacetate. The concentrated filtrate was rendered ammoniacal and the glucoside was precipitated with tannic acid. The precipitate was washed with water and boiled with alcohol in presence of zinc oxide. After evaporation of the alcohol the residue was extracted with absolute alcohol and coloring matter was precipitated from the concentrated solution by the addition of ether. The filtrate from this contained his active glucoside principle which he named adonidin. The chemical work is entirely indefinite, but the pharmacology of this preparation was well worked up. Cervello found that "adonidin" was ten times as active as a preparation Digitoxin(?) used by Koppe[3] in bringing about heart rest in frogs. In contrast to this we find that dosage of adonidin (Merck) given as high as 0.03 g. which is about fifteen times the dose for the digitoxin and about equal to that given for the mixed glucosides from digitalis seeds.

Kramer[4] worked up a parcel of *Adonis aestivalis* by extracting with 96% alcohol and adding an equal volume of water to the extract. This mixture was shaken with petroleum ether, ether, and with chloroform. The chloroform extract yielded an active glucosidic principle which could be precipitated from concentrated alcoholic solutions by the addition of

[1] "Dissertation," St. Petersburg (1880).

[2] *Arch. exp. Path. Pharm.*, **15**, 235 (1882).

[3] R. Koppe, *Ibid.*, 3 (1879).

[4] *Arch. Pharm.*, **234**, 452 (1896).

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ether. He ascribed to his preparation the formula $C_{25}H_{40}O_{10}$, and to this is also assigned the name adonidin according to Abderhalden's Handlexikon,[1] but this is incorrect as there is a marked difference in the action of this principle with the one obtained from *Adonis vernalis*. Thus when a preparation of adonidin prepared from the latter plant by Merck was compared by Kobert with Kromer's preparation it was found that 0.04 mg. of the preparation by Merck, subcutaneously injected into the frog, brought about the typical heart rest and killed the frog in $^3/_4$ hr., while 200 times this quantity of Kromer's preparation failed to bring this about.

Mordagne[2] stated that he obtained only two grams of adonidin from 10 kg. of *Adonis vernalis*. This amounts to only 0.02% of the drug. He reported the results of his analyses as showing, C = 42.6%; H = 7.75%.

More recently several further reports on pharmacological studies have been reported by Fuckelman,[3] Slovtzov,[4] Chevalier,[5] and Mercier,[6] Although it has been recently stated that crude adonidin has been shown to be a mixture, nothing definite has been isolated. These recent papers also disagree among themselves as to the proper method for classifying the drug, some comparing adonis with digitalis, others with squill. References may be found in the medical literature recording the use of this drug in cardiac dropsies and in epilepsy. In the form of the common fluid extract *Adonis* is included in the new National Formulary, where the average dose is given as 0.125 mil or about 2 minims.

Our attention was directed to this plant when, in the process of manufacturing the tincture, a standard seemed desirable. Recent work by Hatcher and Brody,[7] using the intravenous cat method for purposes of determining relative toxicity, showed that the relation between adonidin and ouabain approximated 30:1, respectively. Two lots of drugs, one of which cost four times as much as the other, were made up into tinctures by cold percolation (10 g. per 100 cc.). These were assayed by the one-hour frog method[8] which is official for tinctures of digitalis, strophanthus, and squill. The hearts stopped in systole in a manner similar to that observed when poisoned with digitalis.

From this table it is seen that the average toxicity of tinctures made with more dilute alcohol is somewhat greater than when 95% alcohol is used; also the tinctures prepared with 95% alcohol proved to be more

[1] *Biochem. Handlex.*, **2**, 639 (1911).
[2] *Pharm. J. Trans.*, **16**, 145 (1885).
[3] *Chem. Zentr.*, **1**, 430 (1912).
[4] *Russki Vratch*, **2**, 1 (1913).
[5] *Zentr. Biochem. Biophys.*, **15**, 208.
[6] *Ibid.*, **16**, 652.
[7] *Am. J. Pharm.*, **82**, 360 (1910).
[8] *U. S. Pharmacopoeia*, **9**, 606 (1916).

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stable when examined in this manner. The average M. S. D.[1] of a tincture of *Adonis vernalis* (95% alcohol) we may put at 0.0045 cc. per g. frog. In all these assays the varying resistance of the frogs was taken into consideration, as the M. S. D. for each lot was determined, using crystalline ouabain.

Sample.	Menstruum. % alcohol.	1st assay. Mil.	Time elapsing. Days.	2d assay. Mil.	Loss %.
A.....	50	0.0027	205	0.0039	31
A.....	60	0.004	205	0.005	20
A.....	70	0.0033	205	0.0039	16
A.....	80	0.0033	210	0.0039	16
A.....	95	0.0043	315	0.005	14
A.....	95	0.0043	...	..	..
B.....	50	0.0032	...	..	..
B.....	50	0.0043	...	..	..
B.....	95	0.0055	196	0.006	9
B.....	95	0.0045	...	..	..

Adonis vernalis is therefore more potent than digitalis in terms of this assay process.

Ouabain = $0.0_{3}5$ g. per g. frog.
Digitalis leaves = $0.0_{2}6$ g. per g. frog.
Adonis vernalis leaves = $0.0_{2}45$ g. per g. frog.
Strophanthus = $0.0_{3}6$ g. per g. frog.

It would therefore appear reasonable to adopt the same standard for both these drugs; *i. e.*, 0.006 cc. of the tincture per g. frog.

Turning our attention to the active principle adonidin, we examined two samples procured from Merck. The first, which had been obtained in a sealed tube a number of years ago, appeared to be the product of Cervello's process. It had a dark, molasses-like consistency, and was amorphous and hygroscopic. It is stated in the Index (1902) to be prepared from the herb (kraute). The more recent sample was a brownish yellow amorphous, hygroscopic powder. Merck's new Index (1907) states that it is prepared from the root of *Adonis vernalis* L. and other species of *Adonis*. The material is a mixture melting very indefinitely, softening at 97°, but did not run down at 133°, where decomposition began.

Tests on Merck's Adonidin.—For glucosidic character: 0.4024 g. was dissolved in 50 cc. water. Of this solution 25 cc. gave no reduction directly with Fehling's solution. The other half was heated with 5.5 cc. 38% hydrochloric acid for one hour. The solution was neutralized. Examined by the Walker-Munson process, 0.1066 g. Cu_2O equivalent to 0.0462 g. glucose was obtained. Thus 22.9% glucose (?) was liberated.

The M. S. D. determined by the one-hour frog method was $0.0_{3}5$ g. per g. frog.

These values obtained by pharmacological assaying indicate the presence of approximately 1% of an active constituent, assuming, of course, that the adonidin of Merck is present in the leaf.

[1] Minimum quantity dose producing permanent systole of the frog's ventricle at the end of exactly one hour.

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Our further work in the endeavor to isolate a toxic glucoside proved that the presence of a glucoside in the leaf is questionable. We have shown that a very considerable proportion (over 60%) of the toxicity can be accounted for in the basic fraction precipitated with phosphotungstic acid. Even by acid hydrolysis of fractions of the various plant extracts (which should contain a glucoside if such were present) we obtained but the slightest evidence of the presence of "adonidin." It appears to us that the tannic acid precipitate of Cervello, Mordagne and others who worked with the leaves, were amorphous, hygroscopic mixtures, containing basic substances. While the use of tannic acid as a precipitant for glucosides has been of advantage in many instances; *e. g.*, strophanthin, antiarin, there will also be found described in the literature as glucosides a number of substances precipitated from plant extracts with tannic acid, which are doubtless mixtures.

Our sample consisted of the herbaceous parts in the flowering state and was of German origin (Leipsig).

The proximate analysis shows that the air-dried leaves contained 8.14% moisture, and 10.2% ash. Ligroin extracted 1.78%; ether, 2.5%; and alcohol, 18.6%. The residue insoluble in alcohol had the following composition: crude fiber, 18.65%; pentosans, 14.2%; protein, 14.1%; starch, 1.1%; dextrin, 0.5%. The resin amounts to 3.37%.

The products present in the alcoholic extract and soluble in water yielded, when shaken with ether, a neutral substance melting at 133° and agreeing in composition with formula $C_{14}H_{18}O_4$. The aqueous solution yielded a heavy lead subacetate precipitate. When this was decomposed we were able to prepare from it a yellow complex acidic substance agreeing with the formula $C_{31}H_{32}O_{16}$. It did not melt when heated to 285°, browning at 240°. It formed a beautifully crystalline decacetyl derivative $C_{31}H_{22}O_6(C_2H_3O_2)_{10}$, melting sharply at 190–192°. The filtrate from this lead salt yielded 1.2% levulose, 2.9% adonitol,[1] and lastly choline, $C_5H_{15}O_2N$.

The ligroin extract of the resin yielded a quantity of phytosterolin, and a mixture of a hydrocarbon and of a higher alcohol which had the melting point of myricyl alcohol, 81–83°. The phytosterol fraction consisted chiefly, but not entirely, of a sterol melting at 138–9°, and possessing the formula $C_{27}H_{46}O$. The corresponding acetate melts at 127–128°. The fatty acids were made up to a very large extent of palmitic and linolic acids.

The ether extract of the resin yielded in the usual manner a pure sample of phytosterolin, $C_{32}H_{56}O_6$, melting at 285–295° and forming an acetate which melted at 167–168°.

The chloroform extract of the resin yielded a further quantity of phytosterolin.

[1] Merck, *Archiv. Pharm.*, 231, 127 (1892).

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The ethyl acetate and alcoholic extracts of the resin yielded little of interest, a small quantity of adonitol being isolated, which had apparently adhered to the resin.

The presence of aconitic acid, which was reported by Linderos,[1] we were unable to confirm.

EXPERIMENTAL.

A. Proximate Analysis.

Quantitative extractions of the air-dried leaves with various solvents gave the following results:

Extract.	Per cent.
Ligroin (35–55°)	1.78
Ether (110°)	2.49
Alcoholic	18.59

The proximate analysis gave the results tabulated below:

	Per cent.		
Moisture	8.14	Protein	14.1
Starch (diastase)	1.1	Ash	10.2
Pentosans	14.2, 13.95[a]	Dextrin	0.5
Crude fiber	18.65		

[a] On residue after alcohol extraction.

Quantitative estimations on the alcohol soluble carbohydrates resulted as follows:

A large quantity of the drug was exhausted by cold percolation with 50% alcohol. The percolate was concentrated to a comparatively small volume, and precipitated with an excess of lead subacetate solution. The excess of lead was precipitated with sodium phosphate, and then the solution was made up to a definite volume (1500 cc. = 1080 g. drug). 25 cc. of the solution (18 g. drug) were diluted to 50 cc. The reading in a 1 dcm. tube was —1.4° at 23°. Gravimetric estimations upon this solution by the Walker-Munson process gave, respectively, 0.05 and 0.0515 g. Cu_2O with 5 cc. aliquots. Levulose = 1.2%.

When 25 cc. of the above solution were acidified with 2.5 cc. of 40% hydrochloric acid, permitted to stand overnight and then neutralized and made up to a volume of 50 cc., the rotation in a 1 dcm. tube was —0.5°. Gravimetric estimations with Walker-Munson process failed to show any increase in reducing sugars. Sucrose is absent. This is indicative of considerable stability on the part of the glucoside.

The leaves were examined for the presence of alkaloids according to the method which is official for belladonna, but the results were negative.

B. The Solubilities of the Toxic Constituent and the Presence of a Glucoside.

It was shown by Barger and Shaw[2] that in the case of tincture of digitalis a very considerable part of the toxic constituents adhere to the resin which is precipitated by the addition of water. Consequently they are

[1] *Ann. Chem.*, **182**, 365 (1876).

[2] *Pharm. J.*, **73**, 249 (1904).

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not found quantitatively among the water soluble constituents. Thus, in one case, they found $^{25}/_{29}$ of the toxicity in the resin.

This difficulty might be emphasized in the case of *Adonis vernalis* because of the large quantity of resin present. In the following experiments it will be observed that the toxicity resided quantitatively in the water-soluble constituents even after clarifying with lead subacetate.

Attempt to Prepare "Adonidin" by Using Ethyl acetate.—A quantity of the leaves of *Adonis vernalis* was completely extracted with 50% alcohol, and the percolate concentrated to such a volume that 500 cc. was equivalent to 1080 g. of the drug.

One liter of this solution (2.16 k.) was directly precipitated with basic lead acetate solution[1] (1050 cc.). The filtrate and the washings from the lead precipitate was divided into two equal parts, A and B.

A. This solution was freed from lead by the use of Na_2HPO_4; and then the last trace remaining in the filtrate was removed with hydrogen sulfide and filtering. Eight grams of calcium carbonate were added and the solution was concentrated to a volume of 1500 cc. Twenty-five cc. were removed for the estimation of carbohydrates as described above.

The remainder of Solution A was evaporated to dryness at 45–50° and taken up in 2 liters absolute alcohol in which it did not entirely dissolve. The solution was halved at this point, each part (1 liter) being equivalent to 531 g. *Adonis vernalis*.

Pharmacological examination, by the one-hour frog heart process was made upon this solution.

Ten cc. (5.3 g.) diluted to 50 cc., gives a solution 1.06 × tincture strength. The quantity required to stop the frog heart in one hour, per 1 g. frog, was 0.00292 cc. or calculated as tincture, 0.0031 cc.

This extract contained 21.1% of the drug in solution, *i. e.*, 112 g. in 1000 cc.

The toxicity of this material therefore 0.000065 g. per 1 g. frog. The solution contained considerable ash (5.6% drug).

The remainder of this aliquot (518 g. drug) was concentrated to 250 cc. and precipitated with ordinary ethyl acetate. The supernatant fluid was decanted. The precipitate was redissolved in absolute alcohol and reprecipitated with absolute ethyl acetate. The alcoholic-ethyl acetate filtrates were united, concentrated and again treated with absolute ethyl acetate (500 cc.). The liquid was decanted from a small amount of syrup and the process was repeated. Eventually an ethyl acetate solution was obtained which retained 28% of the original toxicity of the drug, the remainder having been lost in the syrupy precipitates insoluble in ethyl acetate. The dissolved solids showed a toxicity of 0.0000056 g. per 1 g. frog.

The material weighed 2.6 g. but it was only very slightly glucosidic,

[1] U. S. Dept. Agr., Bur. Chem., *Bull.* 107 (revised), 40.

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and furthermore, it contained a high proportion of nitrogenous substances. The solution had a volume of 50 cc.

5 cc. (0.2615 g.) gave 0.0029 g. Cu_2O. 5 cc. heated on a boiling water bath for one hour with 50 cc. of approximately 7% hydrochloric acid gave 0.0180 g. Cu_2O. Hence approximately 2.3% glucose was liberated.

5 cc. required by the Kjeldahl method 17.05 cc. 0.05 *N* acid equivalent to 4.6% nitrogen.

Preparation of the "Adonidin" Fraction Using Hydrogen Sulfide to Remove Pb" Instead of Na_2HPO_4.—1.08 kg. drug were percolated to exhaustion with 7.6 liters of 50% alcohol. The green percolate was concentrated to a volume of 500 cc., and precipitated with 1050 cc. lead subacetate solution. After standing overnight the voluminous yellow precipitate was filtered off and washed three times by trituration with water (500 cc., 250, 250). The brilliant yellow filtrate (3.7 liters) was made up to a volume of 5 liters with 95% alcohol and divided in to five aliquots, each of which was saturated with hydrogen sulfide ($^1/_2$ hour), immediately filtered free from precipitated lead sulfide, and at once concentrated. Each aliquot contained 7.56 g. acetic acid at the beginning of the concentration and after concentrating (at 40°) to a volume of 630 cc. 6.88 g. remained.

In order to determine the reducing action on Fehling's solution before conc entra tion, an aliquot was analyzed.

A quantity (equivalent to 1.8 g. *Adonis vernalis* gave 0.0655 g. Cu_2O = 0.0364 g. Cu_2O per 1.0 g. = 1.56% glucose.

The solutions were now concentrated to a syrup and taken up in 95% alcohol (2.5 liters). There ensued a viscous syrupy separation amounting to 30 g. (2.8% of the drug) which consisted in part of calcium sulfate.

The 95% alcoholic solution was analyzed as follows:

Acetic Acid: 8.0 g.; *direct reducing action* with Fehling's: 0.0331 g. Cu_2O per 1.0 g. plant; *reducing action after heating for 1 hr.* with 10% dilute alcoholic hydrochloric 0.0441 g. Cu_2O per g. plant. *Total solids* dried at 100° = 16.8%; dried at 110° = 16.03%. *Ash* = 3.08%. *Toxicity of solution of tincture concentration* = 0.00040 cc. per g. frog.

This 95% alcoholic solution equivalent to 1047 g. solution was concentrated to a syrup and taken up in about 2.5 liters absolute alcohol. A second heavy viscid syrupy mass separated. After standing overnight the clear supernatant alcoholic solution was decanted from the solid (23.2 g.) and concentrated to a syrup, taken up in about 300 cc. absolute alcohol, a little ethyl acetate was added and the solution was put aside in the ice chest. No crystals separated after standing several weeks.

It was concentrated to a syrup and again taken up in absolute alcohol and made up to a volume of 2000 cc. A precipitate (15 g.) separated. The solution at this point should, it would seem, contain the glucoside, and

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the repeated treatment with absolute alcohol should have removed the sugars and other impurities and we should now have a purified preparation of the glucoside (plus the adonitol). We were unable to separate adonitol by direct crystallization.

An examination of the toxicity indicated that 50% of the toxicity had been lost perhaps through the precipitation of the 30.3 + 23.2 + 15 g. of material above mentioned.

The solution (1047 g. drug) contained 120 g. soluble material (11.4%), of which 21.8 g. was ash. 5 cc. (0.3003 g.) diluted to 26.17 cc. showed a toxicity of 0.0079 cc. per 1 g. frog. Toxicity of residue = 0.000092 g. per 1 g. frog, making it actually weaker than before.

Furthermore, this solution, which should contain the glucoside, gives little or no evidence of the presence of a glucoside when examined by the Walker-Munson process.

(1) Direct reduction: 15 cc. gave 0.1144 g. Cu_2O.

(2) Invert reduction: 15 cc. + 10% hydrochloric acid in dilute alcohol heated for one hour on the water bath gave 0.1246 g. Cu_2O. By calculation the inversion has produced 0.0102 g. Cu_2O more equivalent to 0.004 g. glucose. Since 15 cc. represents 7.85 g. plant this represents approximately 0.05% glucose which at most would represent 0.15% of a glucoside.

The acidification of the solution in presence of absolute alcohol yielded a heavy precipitate which gave a positive test for potassium chloride and it also contained traces of sodium, calcium and magnesium.

C. Complete Examination of Alcoholic Extract.

For this purpose 34 k. were exhausted by percolation with cold wood alcohol. The percolate (318 liters) was concentrated under diminished pressure to a volume of 7.85 liters.

This concentrated extract was poured into 16 liters of distilled water and vigorous shaken. A heavy, green, fatty resin separated. After standing overnight the aqueous layer was decanted through a wetted filter paper and the resin was washed with fresh additions of distilled water.

The Examination of the Water-Soluble Constituents.—This solution (22 liters) containing the water-soluble constituents of 34 kg. of *Adonis vernalis* was concentrated under diminished pressure to a volume of 6.25 liters. The concentrated extract was extracted repeatedly with large volumes of ether. The ether was removed from these extractions and the residues found to be small in amount. They were redissolved in absolute ether, and the ethereal solution was washed with water and extracted in the usual manner with solutions of ammonium carbonate, sodium carbonate and of potassium hydroxide, but the amounts were slight and smeary. The ethereal solution after these extractions was allowed to evaporate spontaneously, whereupon a gradual accumulation of colorless plates separated. This product, upon recrystallization from

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alcohol, melted sharply at 133° to a clear oil. This neutral substance amounted to 0.45 g. and agreed in composition with the formula $C_{14}H_{18}O_4$.

0.1317 g. subst. gave 0.0825 g. H_2O and 0.3243 g. CO_2. Found: C, 67.2; H, 7.0. Calc. for $C_{14}H_{18}O_4$: C, 67.2; H, 7.2.

The aqueous solution which had been extracted with ether was now repeatedly shaken with chloroform, which removed 55 g. of indefinite material. The aqueous layer at this point measured 6.8 liters. The distribution of nitrogen in this solution is as follows:

10 cc. required 36.9 cc. of 0.1 *N* acid, equivalent to 0.05166 g. nitrogen.

20 cc. gave, with lead subacetate, a precipitate containing 0.0182 g. nitrogen.

25 cc. gave, when distilled with MgO, 0.04004 g. nitrogen as ammonia.

The distribution of nitrogen is therefore as follows: Total soluble nitrogen = 0.103%; ammonia nitrogen = 0.032%; lead subacetate precipitable nitrogen = 0.018%; nitrogen precipitated with phosphotungstic acid = 0.056%.

A part of the solution (500 cc.) failed to yield any appreciable precipitate with mercuric acetate when separately examined for asparagine, glutamine and allantoine.

An aliquot of the above-mentioned solution, equivalent to 15 kg. of the plant, was extracted with hot amyl alcohol. The material extracted amounted to approximately 50 g. and failed to yield anything of interest upon further investigation.

The aqueous solution was now diluted to a volume of about 10 liters and precipitated with an excess of basic lead acetate. After standing 24 hours, the bright yellow precipitate was filtered off on suction and washed by agitation with several liters of distilled water and again filtering. The precipitate was suspended in about 20 liters of water and decomposed by saturation with hydrogen sulfide. The filtrate from the lead sulfide was concentrated to a volume of about 500 cc. and permitted to stand for several months. Ten grams of a canary yellow substance separated and was filtered off on suction. This material was treated with boiling water and after filtration treated with boiling 95% alcohol. It was dissolved in pyridine and fractionally precipitated by two additions of anhydrous ether. The first fraction precipitated as an oil but solidified to a crystalline deposit on standing. It had a slightly dirty yellow color. It was dissolved in pyridine, and alcohol was added and the brownish yellow colored crystals which deposited were digested with ether, dried at 150–160° and analyzed (C = 57.0; H = 4.58). The second fraction was a pure lemon-colored precipitate that formed plates on standing. These crystals contained pyridine of crystallization. After digestion with ether and subsequent filtration they were dried at 150–160° and analyzed.

I. 0.1787 g. subst. gave 0.3713 g. CO_2 and 0.0722 g. H_2O, C = 56.66; H = 4.53.

II. 0.1113 g. subst. gave 0.2310 g. CO_2 and 0.043 g. H_2O, C = 56.6; H = 4.34.

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III. 0.5296 g. crystals dried *in vacuo*, lost 0.0805 g. pyridine at 150–160°, C_5H_5N = 15.2%.

Calc. for $C_{21}H_{20}O_{16}$: C = 56.5; H = 4.6.
Calc. for $C_{21}H_{20}O_{16}$: C = 56.3; H = 4.8.
Calc. for $C_{15}H_{16}O_8$: C = 55.5; H = 4.9.
Calc. for $C_{21}H_{22}O_{16} + 1.5C_5H_5N$: C_5H_5N = 15.2%.

The acid decomposed indefinitely, depending on the rate of heating. The pyridine solution, diluted by the addition of water, gave a dark olive-green color with a solution of ferric chloride; with normal lead acetate a yellow lead salt precipitated voluminously. Determination of methoxy group by the Perkin process proved negative.

In the meantime the main filtrate from which the above described yellow substance had separated gradually deposited during several months 7.9 g. further of this substance (C = 56.5; H = 4.8). This product was acetylated, by dissolving in a minimum quantity of pyridine, adding an excess of acetic anhydride and boiling on a reflux for two hours. The crude acetate is precipitated upon the addition of water. It crystallizes from alcohol in rosets of radiating needles, but many crystallizations are required to raise the melting point from 185–190° to a sharp melting point at 191–2°. Acetylization, using acetic anhydride and sodium acetate, did not proceed as smoothly.

The determination of the acetyl radicals was made by Perkin's[1] process.

0.2 g. required 18.5 cc. 0.1 *N* alkali to neutralize acetic acid. Found: 54.6%. (The yellow substance was recovered.)

0.1007 g. gave 0.2094 g. CO_2 and 0.0457 g. H_2O. Found: C = 56.7; H = 5.08.

Calc. for $C_{51}H_{50}O_{26}$: C = 56.75; H = 4.7; $10(C_2H_3O_2)$ = 54.7; $C_{51}H_{52}O_{26}$: C = 56.7; H = 4.9; $10(C_2H_3O_2)$ = 54.6.

The acetate is a deca-acetate, $C_{31}H_{22}O_6(OCOCH_3)_{10}$. The material is not glucosidic. It is insoluble in cold aqueous alkali. An alkaline fusion revealed nothing of interest.

The filtrate from this yellow substance (containing 296 g.) did not contain tannic acid. The solution was made up to 570 cc. and of this 150 cc. was diluted to 300 cc. and enough sulfuric acid was added to make the concentration 5%. Upon boiling for several hours 1.5 g. of the yellow substance separated. Further boiling yielded only resin and some calcium sulfate. The aqueous liquors yielded nothing of interest, except a trace of an osazone. An alkaline hydrolysis with 10% potassium hydroxide for two minutes resulted negatively.

The yellow substance is an alteration product, but not of a glucoside:

Some of the yellow lead salt was washed repeatedly with large volumes of water until the washings were free from sugar. The precipitate was then suspended in 6 l. water and decomposed with hydrogen sulfide. The lead sulfide was filtered off, the

[1] *J. Chem. Soc.*, **87**, 107 (1905). We repeated this on a 1.0 g. sample using 0.5 *N* solutions. There was required 19.2 cc. 0.5 *N* alkali. Found: $(C_2H_3O_2)$ = 56.6%. $C_{21}H_{21}O_5(C_2H_3O_2)_{11}$: requires 57.8%.

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filtrate was concentrated, and hydrolyzed with 5% H_2SO_4. The sulfuric acid was removed quantitatively. By the Walker-Munson process it was estimated that this solution should contain 10.1 g. sugar, it being strongly reducing. This reduction is not due primarily to glucose, because upon examining this syrup it was possible to isolate but a trace of *d*-phenylglucosazone decomposing at 207–208°.

The filtrate from the basic lead acetate precipitate was freed from the excess of lead with hydrogen sulfide, and after filtering off the lead sulfide the filtrate was concentrated to a syrup that measured 1200 cc. Nothing could be separated from this solution in the crystalline condition.

A portion (25 cc.) was examined for sugars. With phenyl hydrazine a crystalline deposit amounting to about one gram of *d*-phenylglucosazone was obtained. The melting point upon recrystallization was 210°. Pentose sugars could not be detected.

Another portion (545 cc.) equivalent to 6.8 kg. of the drug was precipitated with an excess of phosphotungstic acid in the presence of 5% sulfuric acid, and a heavy precipitate resulted. This was removed by filtration and washed with 5% phosphotungstic acid wash and decomposed by the method of Wechsler. The solution of the bases was concentrated to a small volume and digested with absolute alcohol. A considerable quantity of insoluble material was removed by filtration and the filtrate was again evaporated to dryness and treated as before. The absolute alcoholic solution was acidified with hydrochloric acid, but after prolonged standing no crystals separated and the solution had become concentrated to the consistency of a syrup. This residue was fractionally extracted with absolute alcohol.

The first extract of most readily soluble substances was fractionally precipitated with a saturated alcoholic solution of mercuric chloride and the 1st and 3d fractions were crystalline, while the intermediate fraction was smeary.

The first fraction of the crystalline mercuric chloride was dissolved in water and the solution was filtered in order to remove a small amount of brown amorphous material This solution yielded three successive crops of prismatic crystals, which were decomposed with hydrogen sulfide. The filtrate from the mercuric sulfide was allowed to evaporate to dryness over lime in a desiccator. The crystalline residue consisted in each case of needles, which were very soluble in water and in alcohol. They were identified as choline chloride by the analysis of the chloroplatinate that melted upon rapid heating at about 236–238°.

Calc. for $(C_5H_{14}ON)_2PtCl_6$: Pt 31.66. Found: I, Pt, 31.15; III, 31.4.

The third crystalline precipitate of mercuric chloride above mentioned was likewise shown to yield choline chloroplatinate. (Found: Pt, 31.3.) The total yield of choline amounts to about 1.7 g., or approximately 0.025% of the drug.

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A third portion of the syrupy filtrate from the basic lead acetate precipitate (freed from lead) amounting to 7.9 kg. of the drug, was sharply concentrated and then taken up as completely as possible with boiling 95% alcohol. The solution was again evaporated to dryness under diminished pressure in order to remove any water. The residue was boiled with two liters of absolute alcohol and, after standing, the clear, hot supernatant liquid was decanted from the syrup which proved insoluble. The syrup was treated in the same manner with three further portions of absolute alcohol.

From these alcoholic solutions there separated a quantity (about 190 g.) of a crystalline adonitol, which was previously reported by E. Merck.[1] It was shown by E. Fischer[2] to be the pentahydric alcohol obtained by the reduction of ribose. The melting point without crystallization was 98–102°. Our yield was 2.4%. Merck reported about 4.0%.

These alcoholic solutions, after bringing the adonitol to separate as completely as possible, were examined for glucosides. The first extract was made quantitatively to a volume of 300 cc. Its examination pharmacologically by the one-hour frog method, indicated that the preceding extensive operations had deprived this solution of its activity.

A solution made so that it represented fluid extract strength gave: M. S. D. = 0.0086 cc. and 0.0085 cc., whereas an active fluid extract should give M. S. D. = 0.00045 cc. The fraction retains only 5% of the activity.

The second alcoholic extract was still less toxic, and the third was inactive.

The first fraction was slightly acidic. The syrup when dissolved in water yielded an abundant precipitate, when ammonia and tannic acid were cautiously added, but upon treating this precipitate with freshly prepared lead oxide in the usual manner, no "adonidin" resulted, the lead apparently combining with the acidic product under examination.

The syrup, insoluble in absolute alcohol, yielded nothing crystalline. When distilled with hydrochloric acid it could be shown to yield a small quantity of furfural, as phloroglucid could be precipitated in the distillate.

Toxicity of the Base Fraction.—The substances precipitated with phosphotungstic acid were re-examined quantitatively in order to see if we could in this fraction account for any part of the characteristic action of the drug on the frog heart. This work indicated that over 60% of the toxicity is found among the basic substances.

Solution B (see page 441) representing 1080 g. of the drug was evaporated to dryness, taken up in alcohol. A heavy precipitate was separated and the alcoholic filtrate was concentrated at 40–45° to a syrup. It was again taken up in absolute alcohol and another precipitate was filtered off. The solution was concentrated and an unsuccessful

[1] *Loc. cit.*

[2] *Ber.*, **26**, 633 (1893).

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effort was made to quantitatively separate adonitol by prolonged standing in the ice chest. The solution was made to a volume of 2 l.

Five cc. were diluted to 20 cc. (1.35 × tincture). This gave M. S. D. = 0.0059 cc. per g. frog. Or calculated to tincture strength M. S. D. = 0.00797 cc. The alcohol was removed, the syrup taken up in 5% sulfuric acid, and the bases were precipitated with phosphotungstic acid in the usual manner. The bases were liberated with baryta and the solution thereof made up quantitatively to a volume of 500 cc. (1075 g. drug).

This solution gave M. S. D. = 0.0006[1] cc. per g. frog. Calculated to tincture strength we have M. S. D. = 0.013 cc. per g. frog; *i. e.*, 61% of the toxicity of the solution resides in this fraction.

25 cc. (53.75 g. drug) required 21.4 cc. 0.1 *N* acid by the Kjeldahl process, equivalent to 0.03 g. *N* or 0.056%.

This fraction contained 14.4 g. of solids (dried at 100°). The ash amounted to 3.24 g. The fraction yielded a precipitate with tannic acid which was soluble in ammonia.

Several other efforts were made to prepare fractions of the water-soluble constituents which might contain the toxic substance in higher concentration. We endeavored to extract it from the aqueous liquor after defecating with lead subacetate solution. This process was used by Tahara[2] to separate adonin from *adonis amurensis*. An aqueous solution, defecated with lead subacetate solution and then treated with sodium sulfate and containing the extractives from 7.47 kg. drug in a volume of 1.9 liters was repeatedly extracted with large volumes of chloroform (12 liters). The chloroform was dried by shaking with sodium sulfate, concentrated to a syrup in the presence of some calcium carbonate, and then taken up in absolute alcohol. The extracted matter, which had a very unpromising appearance, weighed 5.4 g. When dissolved in alcohol and diluted so that the solution represented the concentration of a tincture it was found that M. S. D. = 0.016 cc. per g. frog. This material reduced Fehling's solution directly. Heating with acids increased its reducing power. This material is exceedingly active in producing the stoppage of the frog heart. ($0.0_5 12$ g. per g. frog = M. S. D.) After standing for months, drying over sulfuric acid, the activity remained practically unchanged. This substance was not precipitated with tannic acid but gave a heavy test with phosphotungstic acid.

The process of salting out with ammonium sulfate, which Thoms[3] used to separate strophanthin, was unsuccessfully attempted.

Cervello's work was repeated and an amorphous product, somewhat more toxic than commercial "adonidin," resulted. When hydrolyzed with dilute hydrochloric acid it did not appear to be entirely glucosidic. However, the material failed to give a test with phosphotungstic acid and nitrogen was present to the extent of only 0.3%.

[1] Contains 0.000017 g.

[2] *Ber.*, **24**, 2581 (1891).

[3] *Ibid.*, **31**, 271 (1898).

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The ground leaves (2 kg.) were exhausted by percolation with 14 liters of 50% alcohol. This percolate was concentrated to a volume of 6 liters and 2.16 liters of lead subacetate solution was added. The yellow lead salt was filtered out on a Büchner, washed with water and to the filtrate 240 g. of sodium phosphate was added. The filtrate and washings from the lead phosphate measured 8730 cc. The solution examined pharmacologically showed a toxicity of 0.0057 cc. per g. frog when diluted to tincture strength.

This solution was concentrated at 50° to a volume of approximately 750 cc., 1.5 cc. of 1% ammonia water was added and a complete precipitation effected with 19.6 cc. of 20% tannic acid solution. The light precipitate was filtered off, washed with water, and triturated with freshly precipitated zinc oxide. The mixture was dried in a vacuum and then digested with cold 95% alcohol. The alcoholic filtrate and washings was concentrated to a syrup and made to a volume of 25 cc. with absolute alcohol.

The solution contained 2.43 g. Toxicity = 0.00003 cc. per g. frog. This represents 24% of the total toxicity of the drug. This volume of solution contains $0.0_{5}29$ g. Cervello's "adonidin."

0.559 g. required by the Kjeldahl process 1.2 cc. 0.1 *N* acid = 0.3%.

0.224 g. gave with the Munson-Walker process 0.0042 g. Cu_2O, equivalent to 0.79% sugar calculated as glucose(?).

0.224 g. heated with dilute alcoholic hydrochloric acid (10%) gave on reduction 0.0438 g. Cu_2O. The sugar split off calculated as glucose amounts to 0.0167 g. or 7.5%.

The residue from the cold 95% alcoholic extract above described was extracted with boiling 95% alcohol and 1.388 g. further was obtained. The material was similar to that obtained by cold extraction. The material showed a toxicity of $0.0_{5}37$ g. per g. frog.

The Examination of the Resin.—The resin which precipitated when the alcoholic extract was poured into water weighed about 1146 g., equivalent to 3.37% of the drug. This resin was redissolved in alcohol and then poured upon purified sawdust, dried, and transferred to a continuous extractor and extracted with the following results:

Petroleum ether (40–60°)	740 g.
Ether	124
Chloroform	85
Ethyl acetate	14
Alcohol	90
Total	1053

The Ligroin Extract.—One-half (370 g.) of this fraction was dissolved in ether and shaken with solutions of potassium hydroxide (5% and 10%). The alkaline solutions were acidified and extracted with ether. On extracting the ethereal solution with ammonium carbonate an emulsion formed. The solution was filtered and a small quantity of a black gummy solid was obtained. This was washed with dilute alcohol and the residue crystallized from dilute pyridine. The resulting crystals were well washed with alcohol and ether and again crystallized from dilute pyridine. It

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gave the characteristic color tests for phytosterolin. It melted at 275–285°. It weighed about 0.43 g.

The material soluble in ammonium carbonate consisted of 20 g. of a blackish green resin from which nothing was isolated.

The ethereal solution was now extracted with solutions of potassium carbonate, and the fatty acids occurring free in the plant were removed. The alkaline extract containing the potassium salts of these fatty acids was acidified and extracted with ether. The ether was removed and some resin was removed by dissolving the residue in petrolic ether. The petrolic ether was dried over anhydrous sodium sulfate. The ether was removed and a residue of about 130 g. was obtained. This was distilled under diminished pressure. The iodine number of the distilled acids which solidified in the receiving tube was found to be 94.4. A very considerable quantity of this material (33 g.) could not be distilled and it remained as a tar in the flask. These fatty acids were studied in connection with those obtained upon the subsequent hydrolysis of the glycerides.

The ether solution which had been extracted with ammonium carbonate and potassium carbonate was now extracted with a solution of potassium hydroxide. On acidification a slight amount of tarry material was obtained from which nothing of a crystalline nature was isolated.

The original ethereal solution of the fat which had been extracted with solutions of potassium hydroxide was evaporated to dryness and the residue, which weighed 177 g., was saponified by boiling with 10% alcoholic potash for four hours. The alcohol was removed and water added to completely precipitate the unsaponifiable material, which was extracted with ether.

Examination of Unsaponifiable Matter.—The dried solution was evaporated to dryness and the residue was an orange-colored heavy viscid oil amounting to 56 g. It was dissolved in absolute alcohol (1.5 liters) and upon standing a small amount of amorphous material separated. The melting point was indefinite and suggested a mixture of hydrocarbon and a higher alcohol. By means of the phthalic acid fusion and subsequent extraction with sodium carbonate a small quantity of a hydrocarbon melting at 63–65° was isolated. Five crystallizations from ethyl acetate raised this melting point to 68–69°, the last traces running down the tube at 72°.

Calc. for $C_{31}H_{72}$: C, 85.4; H, 14.6. Found: C, 84.4; H, 14.4.

The poor melting point and low results of the combustion indicate that this was possibly pentriacontane contaminated with some alcohol.

A small quantity of sodium salt of an acid phthalic ester was isolated and boiled with alcoholic potash. A product separated which had the melting point of myricyl alcohol, 81–83°.

After the separation of the mixture of hydrocarbon and alcohol, the solu-

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tion of the unsaponifiable material was concentrated and crystalline material weighing 6.1 g. was obtained. This was subjected to a fractional crystallization from alcohol. The more soluble fraction from alcohol was acetylated and the acetyl derivative, melting at 119–121°, subjected to many crystallizations from a mixture of ethyl acetate and alcohol. By this means beautiful crystalline rods of the acetate melting at 127–128° were obtained.

0.1979 g. of the anhydrous acetate made up to 20 cc. with chloroform showed a rotation of —0.76° in a 20 cm. tube, whence $[\alpha]_D^{23} = -38.5°$.

The phytosterol was regenerated from its acetyl derivative and after crystallization from alcohol it was burned. M. p. 138–139°. It was dried to constant weight at 115°.

Calc. for $C_{27}H_{46}O.H_2O$: H_2O, 4.8. Found: H_2O, 3.8.

Calc. for $C_{27}H_{46}O$: C, 83.9; H, 11.9. Found: C, 83.5; H, 12.1.

0.1732 g. of the anhydrous phytosterol made up to 20 cc. with chloroform showed at 23°, a rotation of —0.62° in a 20 cm. tube, whence $[\alpha]_D^{23} = -36°$.

The most insoluble fraction of the unsaponifiable material from alcohol yielded an acetyl derivative, crystallizing from ethyl acetate and alcohol in beautiful plates, melting at 119–120°. This was shown to be a mixture of the ordinary phytosterol ($C_{27}H_{46}O$) and another of lower carbon content. Lack of material prevented the isolation and subsequent identifications of this.

The syrupy mother liquor remaining after these substances had been isolated was freed from alcohol and subjected to a fractional distillation. It passed over between 190° to 320° at 15 mm. pressure. Most of the fractions were thick, sticky oils which did not solidify on cooling. The fraction distilling at 270° to 320° partially solidified and after several crystallizations from ethyl acetate and alcohol gave crystalline material similar to the above described mixture.

Examination of the Fatty Acids.—The alkaline solution from which the unsaponifiable matter had been extracted with ether was acidified and the liberated fatty acids were extracted with ether. The ether solution was dried over sodium sulfate and then the ether was removed and the residue distilled under diminished pressure. These boiled chiefly at 230–280° at 20 mm. The weight of the distilled acids was 36 g. and the iodine number was 110.3.

These acids were mixed with those which had been extracted with potassium carbonate solution. Two portions weighing 20.5 g. each were converted into the lead salts, which were treated with ether in the usual manner. Liquid acids equivalent to 64.7% and 66.8% of the total acids were obtained.

The lead salts of the fatty acids, insoluble in ether, were decomposed with hydrochloric acid and the solid fatty acids separated in the usual

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manner. These were taken up in ether, dried over sodium sulfate and the solvent removed.

These dried fatty acids were then esterified by the method outlined by Phelps and Phelps.[1] The dried acids were dissolved in absolute methyl alcohol containing 2% hydrochloric acid and to which fused zinc chloride was added. Through this mixture during the interval of about one hour was driven absolute methyl alcohol. The crude ester was then taken up in ether extracted with potassium carbonate solutions, washed, dried and the solvent removed. By this procedure average yields of 93% of the ester were obtained.

The methyl esters of the solid acids practically all distilled under 205° at 20 mm. pressure. Most of the acid came over at 195–200° at 20 mm. pressure. These were distilled several times.

Palmitic acid melting at 61–62° was isolated.

Calc. for $C_{16}H_{32}O_2$: C, 75.0; H, 12.5; N. V., 219.1. Found: C, 75.0; H, 12.3; N. V., 210.9.

The unsaturated acids were regenerated from their lead salts soluble in ether and converted into their methyl esters. The latter were fractionally distilled 6 times under 20 mm. pressure when the following fractions were obtained:

Fraction I (b. p. —215°). This fraction was the largest containing about 80% of the acids. It gave analytical results corresponding to impure methyl linolate.

Calc. for $C_{19}H_{34}O_2$: C, 77.5; H, 11.5; I. V., 172.7. Found: C, 77.8; H, 114; I. V., 160.3.

Oxidation with potassium permanganate in the usual manner yielded a small quantity of sativic acid melting at 155–160°.

Fraction II (b. p. 215–218°). This fraction was small, amounting to about 4% of the total liquid acids. It had an iodine number of 160.3.

Fraction III (b. p. 218–222°). This fraction amounted to about 12% of the total liquid acids.

Calc. for $C_{19}H_{34}O_2$: C, 77.5; H, 11.5; I. V., 172.7. Found: C, 77.8; H, 11.3; I. V., 168.1.

The boiling point and analytical data show this fraction to be methyl linolate.

Fraction IV (b. p. 222–226°). This fraction was small, amounting to about 4%. It had an iodine number of 161.1.

The liquid acids are thus shown to consist almost exclusively of linolic acid.

The ether extract of the resin, amounting to about 3 liters, separated 54 g. of smeary resin on standing and as the extraction continued. This was filtered off. The more readily soluble part amounted to 70 g. The

[1] *Am. J. Sci.*, [4] **24**, 194–196 (1907).

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green precipitate was dried and powdered and boiled with several liters of ether for days. The part insoluble in the ether was dissolved in boiling absolute alcohol and 5.5 g. remaining insoluble. Concentration of the alcoholic filtrate yielded about 6 g. further. After crystallization from dilute pyridine several times a light green semi-crystalline product was obtained which was an impure phytosterolin. With much difficulty 3.7 g. of phytosterolin melting at about 285–295°, was obtained.

Calc. for $C_{28}H_{46}O_6$: C, 72.3; H, 10.2. Found: C, 71.9; H, 10.2.

The acetate melted at 167–168°.

0.4919 g. acetate made up to a volume of 20 cc. with chloroform showed a rotation of 1.114° in a 20 cm. tube at 23° whence $[\alpha]_D^{23} = -22.6$.

The ether extract from which the crude phytosterolin had been filtered off was extracted with solutions of ammonium carbonate, sodium carbonate and potassium hydroxide, and then the ether upon evaporation contained but a slight quantity of dissolved substance. The alkaline extracts which contained quantities of chlorophyll yielded nothing of interest upon acidification.

The chloroform extract of the resin amounted to 85 g.

A further quantity of phytosterolin (2.75 g.) was obtained here. Nothing was isolated by alkaline extractions. The fraction was not glucosidic.

The ethyl acetate extract of the resin (14 g.). A small quantity (3.9 g.) of adonitol separated as the extraction proceeded. It melted at 102–3°.

Calc. for $C_5H_{12}O_5$: C = 39.5; H = 7.9. Found: C = 39.3; H = 7.8.

The alcoholic extract of the resin (90 g.). A very small amount of the toxicity was in this fraction. However, the material itself was quite toxic (0.0411 g. per 1 g. frog). An acid and an alkaline hydrolysis failed to yield anything of interest. The solution reduced Fehling's solution directly, but this reduction was increased after heating with aqueous acid.

KALAMAZOO, MICH.

[CONTRIBUTION FROM THE RESEARCH LABORATORY, HERCULES POWDER COMPANY.]

A QUANTITATIVE ESTIMATION OF ACETIC, PROPIONIC AND BUTYRIC ACIDS.

BY R. D. CROWELL.

Received November 19, 1917.

The separation of the lower acids of the acetic series from each other has been accomplished more or less satisfactorily by methods based upon the following principles:[1]

[1] Allen's "Commercial Org. Analysis," 1, 515–519 (1914). Owing to the inadequacy of library facilities it was impossible to consult the original literature on this subject.

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(1) Butyric acid and the higher homologs may be partially separated from the lower members of the series by saturating their aqueous solutions with calcium chloride, the butyric and higher acids rising to the surface as oils.

(2) On partial neutralization and distillation mixtures of valeric and butyric acids may be partially separated.

(3) Mixtures of any two can be estimated by distillation, neutralization with barium hydroxide of known strength and weighing the dried barium salts.

(4) Duclaux claims to be able to estimate quantitatively mixtures of these acids by means of the difference in the rate of distillation of the various homologs.

(5) It has been stated that butyric and valeric acids are extracted from a water solution by shaking with benzene while formic and acetic acids remain in the water. As far as we could ascertain, none of these methods have been found suitable for a routine laboratory analysis for acetic, propionic and butyric acids.

Phelps and Palmer state[1] that the solubilities of quinine acetate, propionate and butyrate in carbon tetrachloride are different enough to be of possible use in the separation of the three acids but give no results of actual experiments.

Experimental.

Thinking it possible that quinine sulfate might be used in a method of analysis the following experimental work was done:

About 0.3 g. of solid barium acetate was dissolved in 25 cc. warm water. 0.6 g. quinine sulfate was added and the resulting mass, containing solid barium sulfate, quinine acetate, and unchanged quinine sulfate was evaporated to dryness at 50° at a pressure of about 15 cm., 75 cc. of carbon tetrachloride were then added to the flask and boiled on a steam bath for 10–15 minutes. The solution was then cooled to 25° and filtered. The residue was thoroughly washed with carbon tetrachloride, bringing the filtrate to a volume of 100 cc. and the filtrate distilled over 20 cc. phosphoric acid. The distillate was titrated with 0.25 *N* barium hydroxide and the equivalent amount of acid compared with that originally present. This was repeated with barium propionate and butyrate with the following results:

TABLE I.

	Amount present.	Amount recovered.	% recovered.
	Butyric Acid.		
1	0.1693 g.	0.1076 g.	63.6
2	0.1692 g.	0.1076 g.	63.6

[1] I. K. Phelps and H. E. Palmer, *J. Biol. Chem.*, 29, 199 (1917).

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TABLE I (*continued*).

	Amount present.	Amount recovered.	% recovered.
	Propionic Acid.		
1	0.1612 g.	0.0975 g.	60.5
2	0.1259 g.	0.0717 g.	60.0
	Acetic Acid.		
1	0.0860 g.	0.0067 g.	7.9
2	0.1720 g.	0.0138 g.	8.0

The butyric acid recovery was too low. After trying (1) excess quinine sulfate, and (2) a mixture of absolute alcohol and carbon tetrachloride, with no better results, this work was abandoned.

The solubilities of barium acetate, propionate and butyrate in alcohol, were then considered, but proved to be too close to one another to permit of a separation of the three acids in this way. The following table gives the results obtained in this experiment:

TABLE II.

Solubilities in 97% C_2H_5OH.

Salt.	Solubilities per 100 cc. 1.	2.	3.	Average.
Barium acetate	0.0730 g.	0.0742 g.	0.0704 g.	0.0723 g.
Barium propionate	0.1616 g.	0.1610 g.	0.1638 g.	0.1631 g.
Barium butyrate	0.1728 g.	0.1662 g.	0.1710 g.	0.1700 g.

A combination of the first and fifth principles cited above was then considered. This consists in the extraction of butyric acid from an aqueous solution, to which a salting agent has been added, by means of an immiscible organic solvent. For this extraction a solvent must be chosen in which acetic acid is relatively insoluble. Obviously the solubility of propionic acid in this solvent does not matter as a mixture of any two of these acids can be readily analyzed as stated under (3).

After trying benzene, toluene, carbon tetrachloride, distillate (high boiling gasoline), gasoline and kerosene, the latter was selected as the organic solvent, first because it extracts a large percentage of the butyric acid, with but little acetic acid, and second because it is relatively safe to handle. (The efficiency of the extraction is increased by the presence of a salting agent in the water layer, calcium chloride being usually used.) After trying a large number of different highly soluble salts a saturated solution of calcium chloride to which has been added a little potassium chloride (20 g. to a liter) was found to be most satisfactory.

Experimental data showing relative solubility of acetic and butyric acids in organic solvent and aqueous layer.

Organic solvent: kerosene 15 cc.

Aqueous solution: 15 cc. saturated calcium chloride—potassium chloride, 1 cc. butyric acid.

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TABLE III.

(1).

Titration in cc. 0.25 *N* Barium Hydroxide.			Percentage Acid in Layers.	
	Water layer.	Kerosene layer.	Water layer.	Kerosene layer.
1	3.2 cc.	40.5 cc.	7.3%	92.7%
2	3.0 cc.	40.8 cc.	6.2%	93.8%
3	3.0 cc.	37.9 cc.	7.5%	92.5%
4	3.0 cc.	38.6 cc.	7.2%	92.8%
5	3.3 cc.	39.7 cc.	8.7%	92.3%
		Average,	7.2%	92.8%

5 cc. 10% Acetic Acid.

(2).

	Water layer.	Kerosene layer.	Water layer.	Kerosene layer.
1	35.1 cc.	0.90 cc.	97.5%	2.5%
2	31.0 cc.	0.75 cc.	97.7%	2.3%
3	37.6 cc.	0.92 cc.	97.6%	2.4%
4	37.4 cc.	0.70 cc.	98.2%	1.8%
5	36.1 cc.	0.80 cc.	97.8%	2.2%
		Average,	97.7%	2.3%

With the total acidity of a sample and the total weight of CH_2 groups present known, the accuracy of the determination of all three acids depends on the accuracy with which the butyric acid present can be determined. By assuming that the kerosene layer contains only propionic and butyric acid, after being shaken with all three acids in the salting solution, and by analyzing this solvent layer for the butyric and propionic acids by means of the total acidity and a salt weight there is obtained a value for the butyric acid which will vary a more or less definite amount from the true butyric acid content. This factor depends upon the manipulation of the method and solubility in water layer, etc., and will be considered after the outline of the method finally adopted, which follows.

The accuracy of the method depends to a great extent upon the desiccation of the salts. The barium salts, if much propionate is present, are not satisfactory, even if desiccated for 40 hours or more in a high vacuum at 100°. The sodium or potassium salts if weighed in tared squat weighing bottles (60 by 30 mm.), after heating 12 hours at 200°, proved to be the most satisfactory.

Method.

An amount of sample equivalent to about 7.5 g. of acid is diluted or concentrated to 250 cc. (in a volumetric flask). This is the standard sample.

(1) A 50 cc. sample of this is pipetted into a 200 cc. precipitating jar and 2.5 cc. of 50% sulfuric acid is added (to prevent the precipitation of

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silver acetate, etc.). Then, sufficient solid silver sulfate is added to precipitate all the chlorides present. This is then stirred with an electric stirrer (one such as used at soda fountains is very satisfactory) until when filtered it shows an excess of silver when tested with hydrochloric acid. It is filtered and 25 cc. of the filtrate are pipetted into a 250 cc. florence flask. 20 cc. 33% phosphoric acid and a few bits of brick are added to the flask, which is then connected to a 30 cm. Liebig condenser and a dropping funnel. It is then distilled until the residue amounts to about 20 cc., then 20 cc. carbon dioxide-free water is added by means of the dropping funnel and the distillation continued as before. This is repeated three times to insure complete distillation of volatile acids.

The distillate is caught in a 250 cc. flask and titrated with 0.25 *N* sodium hydroxide using phenolphthalein as indicator. The titrated distillate is boiled down to about 8 cc. and transferred to a tared squat weighing bottle, in which it is evaporated to dryness on a steam bath. The weighing bottle and contents is then desiccated at 220° for 12 hours and weighed.

The total acidity expressed as sodium acetate subtracted from the salt weight gives the weight of CH_2 groups. This figure, multiplied by 4.2, to correct for dilution and size of sample, gives the total weight of CH_2 groups per 100 cc. sample.

(2) A 150 cc. portion of the standard sample is pipetted into a precipitating jar and freed from chlorine, as the 50 cc. portion was in (1). 100 cc. of the chlorine-free filtrate are pipetted into a Kjeldahl flask fitted with condenser and dropping funnel. 20 cc. of 33% phosphoric acid are added and the distillation carried on until 20–22 cc. residue remain in the flask. 20 cc. carbon dioxide-free water are added, drop by drop, and the distillation continued until 20–22 cc. remain again. This is repeated three times. The distillate is caught in a 500 cc. Pyrex flask and titrated with 0.25 *N* barium hydroxide and phenolphthalein. This neutralized distillate is then concentrated to a volume of from 5 to 8 cc. To this concentrated neutralized distillate is added from a buret the equivalent of the 0.25 *N* barium hydroxide titration in 4 *N* hydrochloric acid. Since hydrochloric acid is a much stronger acid than acetic, butyric or propionic, the volatile organic acids are now liberated in a 10 cc. volume.

This concentrated acid solution is carefully poured into a 300 cc. separatory funnel. The flask is then washed with 25 cc. of saturated calcium chloride, saturated with potassium chloride, which is then poured into the funnel. This is repeated with another 25 cc. portion of salting solution and two 25 cc. portions of filtered kerosene. The separatory funnel is well shaken, the butyric acid passing into the kerosene together with

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some of the propionic. On settling, the salting solution layer is run off and discarded. A 10 cc. portion of salting solution is added to the kerosene in the funnel, which is then shaken and allowed to separate into two layers again. This salting solution layer is then run off and discarded, carrying with it practically all of the remaining acetic acid.

To the kerosene in the funnel is now added 150 cc. of carbon dioxide-free water, and the whole titrated with 0.25 *N* barium hydroxide and phenolphthalein with frequent shaking. Barium propionate and barium butyrate being insoluble in kerosene, pass into the water layer as fast as formed by the neutralization of the free acids in the kerosene. Thus, when the end point is reached the water layer may be drawn off into a 250 cc. graduated flask which is filled to the graduation with repeated 30 cc. water washings of the kerosene, and the kerosene discarded.

The whole of this 250 cc. solution is then treated with 12.5 cc. 50% sulfuric acid and 3 g. of silver sulfate as before to free it from chlorine. 200 cc. of the chlorine-free filtrate are pipetted into a Kjeldahl flask and distilled over 40 cc. 33% phosphoric acid, and washed three times with 20 cc. portions of carbon dioxide-free water as with the other distillations. The distillate is caught in a 500 cc. Pyrex flask, titrated with 0.25 *N* sodium hydroxide and evaporated to a 5 to 8 cc. volume, and transferred to tared weighing bottles. It is then evaporated to dryness on a steam bath and dried to constant weight in an electric oven at 200°. This gives the salt weight of sodium propionate and sodium butyrate.

The sodium propionate equivalent of the 0.25 *N* sodium hydroxide titration subtracted from this salt weight gives the weight of CH_2 groups present as butyric acid in the distillate. This value for the butyric acid obtained by multiplying this CH_2 weight by C_3H_7COOH/CH_2 corrected for dilution will not quite equal the true butyric acid content of the sample, since there is a definite proportional loss during extraction. To correct for this a factor F is inserted. This CH_2 group weight must therefore be multiplied by the following factors to give the butyric acid weight in 100 cc. of the standard sample:

F; 1.05, to correct for sulfuric acid addition; 1.25, to correct for aliquot portion taken for distillation; 6.286 = C_3H_7COOH/CH_2.

This butyric acid weight multiplied by $(CH_2)_2/C_3H_7COOH = 0.3142$ gives the weight of CH_2 groups present as butyric acid in 100 cc. of the standard sample. Now, in (1) the total CH_2 groups present as butyric and propionic acid was determined, hence subtracting from the total weight of CH_2 groups present as butyric acid, gives the weight of CH_2 groups present as propionic acid in 100 cc. of standard sample. This weight of CH_2 groups multiplied by $C_2H_5COOH/CH_2 = 5.29$, therefore, gives the propionic acid per 100 cc. sample.

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The acetic acid per 100 cc. is determined as follows:

4.2 times the 0.25 *N* sodium hydroxide titration of the distillate from the 25 cc. sample in (1) gives the cc. of 0.25 *N* NaOH equivalent to the total volatile acid in 100 cc. of the original sample. Now, if the propionic and butyric acid weights per 100 cc. are converted into the equivalent number of cc. of 0.25 *N* NaOH and subtracted from the total volatile acid titration computed above, the difference will be the cc. of 0.25 *N* NaOH equivalent to the acetic acid per 100 cc. of sample.

Determination of F.

Applying the above method, the mean factor F, by which the butyric acid found in the kersene layer is to be multiplied to correct for incomplete salting was next determined.

TABLE IV.

Sample No.	Butyric acid present, g.	Butyric acid found, g.	Factor.	Acid ratio HAc–HPr–HBu.
1	0.9338 g.	0.7685 g.	1.215	0:0:1
2	0.9379 g.	0.8333 g.	1.125	0:1:1
*3	0.9890 g.	0.9209 g.	1.074	1:1:1
4	0.9749 g.	0.8507 g.	1.146	1:1:1
5	1.9630 g.	1.7669 g.	1.111	1:1:1
6	0.1953 g.	0.1713 g.	1.140	3:3:1
7	0.1953 g.	0.1898 g.	1.029	3:3:1
8	0.1953 g.	0.1735 g.	1.125	3:3:1
		Average,	1.120	

Applying the average factor to the analysis, the following data on the accuracy of the butyric acid determination was obtained:

TABLE V.

Sample No.	Butyric acid present.	Butyric acid reported.	Per cent. Error.
1	0.9338	0.8607	7.8%
2	0.9379	0.9333	0.5%
3	0.9890	1.0314	4.2%
4	0.9749	0.9528	2.2%
5	1.9630	1.9789	0.7%
6	0.1953	0.1919	1.7%
7	0.1953	0.2126	8.1%
8	0.1953	0.1943	0.5%
		Average error,	3.2%

To determine the effect of this error upon the estimation of all three acids, samples were run containing various ratios and analyzed for all three acids with the following results:

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TABLE VI.

Complete Analysis.

No.	Present. Hac. %.	HPr. %.	HBu. %.	Total acid. %.	Reported. Hac. %.	HPr. %.	HBu. %.	Total acid. %.	Mean error. %.
1	0.720	0.350	0.195	1.255	0.700	0.380	0.190	1.270	4.7
2	0.720	0.340	0.195	1.255	0.760	0.280	0.210	1.250	7.8
3	0.720	0.340	0.195	1.255	0.720	0.340	0.190	1.250	0.7
4	0.720	0.340	0.195	1.255	0.720	0.330	0.200	1.250	1.5
5	0.631	0.590	0.560	1.782	0.623	0.598	0.566	1.787	1.0
6	0.631	0.590	0.560	1.782	0.679	0.546	0.559	1.784	3.8
								Average,	3.25

NOTE.—Acids used in making up standard samples: (1st) glacial acetic acid, (2nd) propionic acid, prepared by saponifying the ethyl ester, fraction used boiling between 139–142°, (3rd) butyric acid, prepared from the ester, boiling at 161–163°.

SAN DIEGO, CALIF.

NOTE.

Rapid Organic Combustion.—We wish to report here on a method of rapid combustion as it is practiced in our laboratory. There is nothing essentially new in the principle of the method as employed by us. To Dennstedt,[1] to Beck[2] and to Miss Marie Reimer[3] belong the credit of building up the theory and practice of the rapid combustion. However, in our laboratory where the demand made on every furnace is very great and where combustions are made continually, there were many occasions when none of the three methods worked satisfactorily, even when carried out exactly under the original conditions given by their respective authors. In the course of years some of the imperfections of the three methods were corrected, and the advantageous parts of all were combined in one, so that finally we have a combustion tube which served for more than three hundred combustions without change of the catalyst.

Cerium dioxide was employed as the catalyst, as suggested by Beck. It was soon found that when the dioxide was prepared in the manner described by the original authors, samples were obtained that differed considerably in their efficiency. Often the catalyst was exhausted after a very few combustions. On other occasions the dioxide was inactive from the start, and at times an inactive dioxide improved after several combustions, but became exhausted after a few additional combustions. As the same source of cerium nitrate gave samples of dioxide of variable

[1] Dennstedt, M., "Anleitung zur vereinfachten Elementaranalyse," III. Aufl. Hamburg, 1910, p. 66.

[2] Beck, J., *Ber.*, **46**, 2574 (1913).

[3] Reimer, M., THIS JOURNAL, **37**, 1636–38 (1915).

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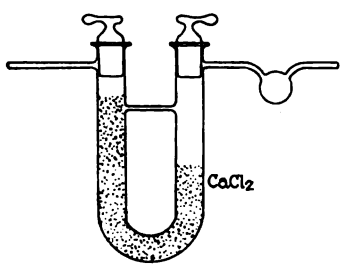
efficiency it was thought that some component of illuminating gas had a deleterious effect on the catalyst. Because of this it was concluded to convert the nitrate into the dioxide in an atmosphere of oxygen. The catalyst prepared in this manner seems to maintain its efficiency indefinitely.

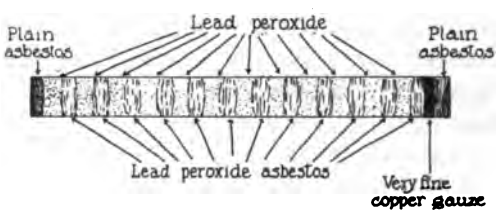
The central part of the tube is filled with copper oxide in wire form. At each end of the copper oxide is placed a charge of cerium dioxide. There is a layer of pure asbestos between the copper oxide and the catalyst, as well as between the catalyst and the neighboring part. An innovation in the tube is a small coil made of very fine platinum gauze. The coil serves as a protection for the boat from copper oxide that might be carried over from the terminal copper coil. Through the presence of this coil it is possible to obtain reliable data, regarding the ash content of a substance.

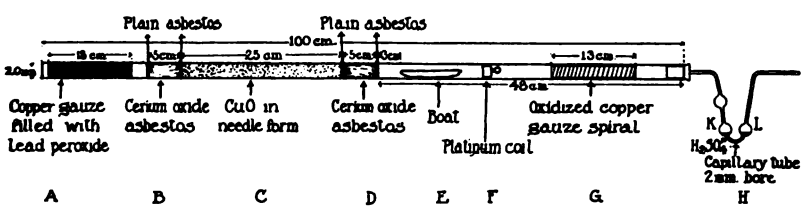
The manner of filling the tube is best seen from the accompanying diagrams.

The Combustion Tubes should be 100 cm. long and 20 mm. in diameter. Where the demand on the furnace is considerable, a tube of transparent quartz was found economical. The combustion tube is connected to any conventional drying train by means of part H. This consists of a capillary tube of 2 mm. bore and of three bulbs, 15 mm. in diameter. The distance between K and L is 25 mm. The section is filled with sulfuric acid.

Absorption Apparatus.—For the absorption of water a U-tube, provided with a bulb for retaining the condensed water as given on the draw-







ing, is recommended. For the absorption of carbon dioxide two usual U-tubes filled with soda lime are employed.

The Lead Peroxide is kept in position in a copper gauze wrapper. Layers

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of pure peroxide alternate with layers of asbestos impregnated with the reagent. For this purpose, the asbestos is mixed with an equal volume of dry peroxide.

Catalyst.—Purified asbestos fiber is suspended in a saturated solution of cerium nitrate, and the mixture is placed on a boiling water bath to remove the greater part of the water. The still moist asbestos is then transferred to a glass tube and is heated in a stream of oxygen. One end of the tube is drawn to a narrow point which is connected with the oxygen supply. The opposite end is provided with a stopper containing a glass tube, which dips into a flask containing dilute alkali.

Rules for Combustion.—The burners under Section A of the tube are regulated so that the temperature in the center of the lead peroxide is kept constant at 300 to 320°. This temperature should be regulated when all the burners are lighted so as to give the maximum heat required by the combustion. Once so adjusted, the burners remain fixed and should not be disturbed so long as the same charge of the tube remains in service. Before beginning the combustion, the absorption apparatus is attached to the tube which is then burned out in a current of oxygen for thirty minutes. At the end of this time the absorption tubes are weighed and again attached to the tube.

The right end of the tube up to two burners to the left of Section D is then allowed to cool to the temperature of the room. At this moment the boat is inserted into the tube. As soon as the boat is in position, the burners are lighted under the right end of Section G and under Section D. It is recommended to cover the furnace over Section D with asbestos board or with brick, to insure maximum heat of the catalyst. As soon as the requisite temperature of the catalyst is developed, it turns light yellow in color. At this stage the burners are lighted under the right end of the furnace close to the right end of Section E. Following that moment the flames are regulated approximately in the same manner as in the Dennstedt combustion. One has to adapt himself to the nature of the substance.

The combustion is terminated when all the carbon in the boat or on the tube in the region of the boat is burned off. On burning usual substances the combustion lasts about 10–15 minutes from the moment when the catalyst reaches the requisite temperature until the end of the operation.

After the combustion is completed the flames corresponding to Section D and to the right of it are turned off and oxygen is passed for 20 minutes. The absorption tubes are weighed immediately. Generally a combustion consumed 45 minutes, including the two weighings.

P. A. LEVENE AND F. W. BIEBER.

THE LABORATORIES OF THE ROCKEFELLER
INSTITUTE FOR MEDICAL RESEARCH.

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NEW BOOK.

The Nature of Matter and Electricity: An Outline of Modern Views. By DANIEL F. COMSTOCK AND LEONARD T. TROLAND. New York: D. Van Nostrand Co. 1917. 203 pp. $2.00 net.

This book is an important addition to "popular" scientific literature, covering an extraordinarily wide range of scientific knowledge with great success.

The text is divided into two parts: the first is a brief outline of the modern theory of matter, electricity and energy, by Professor Comstock; the second and larger part, by Doctor Troland, is an appendix which discusses in fifty-six sections, with further detail, some of the problems touched upon in Part I.

In Part I, Professor Comstock's wide knowledge and charming clarity of expression are most successfully employed, and the text can be recommended without reservation to scientists and laymen alike. Part II is also a successful achievement and will provide the layman with much correct information and a happy insight into the spirit of modern physical thought. For the scientist, however, the second part of the book is marred by a number of statements which, to say the least, do not accord with the most plausible modern views.

Thus, on page 60, we are told that atoms and molecules both are probably pretty nearly spherical. Even if the author of a book published in 1917 were not familiar with the work of Langmuir on the shape of molecules, the commonest facts of organic chemistry should have made him cautious about writing a paragraph which will certainly give the layman the idea that all molecules are nearly spherical. And, furthermore, as to the shape of atoms themselves, the facts connected with the spatial properties of chemical valence, are certainly so important as to make it very undesirable to permit the reader to carry away the idea that the boundary of an atom is a homogeneous spherical shell.

On page 93, we are told that Maxwell may be considered as the founder of kinetic theory which is certainly a little hard on Clausius and others.

On page 95, the impression is certainly given that the kinetic energy of the molecules of *any* substance is proportional to the absolute temperature, which, is as a matter of fact, only true for dilute gases. The variations from the "principle of the equipartition of energy" are indeed so great that the molecules of a solid at low temperatures have practically no kinetic energy at all, although the molecules of a gas at the same temperature would have a large average kinetic energy.

On page 119, we are told that in general, the stronger the internal forces that hold the atoms of a compound together, the greater will be the specific heat, which is manifestly in general not true.

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Other examples of a similar kind might be given. On the whole, however, the book must be considered as a distinct success.

RICHARD C. TOLMAN.

An Elementary Study of Chemistry. By WILLIAM MCPHERSON AND WILLIAM EDWARDS HENDERSON, 2nd revised edition, 576 pages, $1.60. Ginn and Company, 1917.

This is a revision of the first of the three well-known texts by the above authors. It is addressed to classes which have not had a preliminary course in the High School but are old enough to profit by a presentation more advanced than that usually given to college-preparatory students. The authors have attempted "to make the text clear in outline, simple in style and language, conservatively modern in point of view;" and in this they have been eminently successful.

"The question as to what shall be included in an elementary text on chemistry is perhaps the most perplexing one which an author must answer." To this all will agree, especially if to this perplexity be added that of the best arrangement of topics. Some authors have attempted to escape the first dilemma by including everything—an easy method by which the teachableness of the text suffers somewhat from its encyclopedic character. One can not see the trees for the forest. In this, newest of texts, one could wish for less rather than more, but the coördination is so good, the back-references so frequent, that a young student will hardly find himself at loss in the wealth of information.

It is pleasant to find a separate chapter on the fundamental topic "Acids, Bases and Salts; Neutralization;" also one on "Valence"—old fashioned valence!

In regard to sequence, nearly all texts present oxygen and hydrogen first of the elements; but after that there are nearly as many different orders of presentation as there are authors. In this volume, the elements appear thus:—carbon first, then nitrogen, chlorine, sodium, sulfur; then the families of the non-metals; then the metals in the usual order. These chapters are interspersed with others on the fundamental laws and theories of chemistry, so arranged that in each case the foundation for the theory there presented is found in illustrations immediately preceding. In this the text excels; also in the fact that the authors have not been tempted to lead the student too far into those branches of theory which, though suitable for the university student, may be and therefore should be deferred until adequate treatment may be given in, at least, a second-year course.

The size of the volume is more attractive than that of the "Course in General Chemistry" by the same authors. In general appearance the book is one of which the publishers may well be proud. It will doubtless find for itself a broad field of usefulness.

ARTHUR JOHN HOPKINS.

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THE SOLUBILITY OF PURE RADIUM SULFATE.[1]

BY S. C. LIND, J. E. UNDERWOOD AND C. F. WHITTEMORE.

Received November 19, 1917.

1. Introduction.

In the recovery of radium from its ores by various processes, radium is at some stage always precipitated together with barium as sulfate. The completeness of this precipitation involves relationships not only of great practical but of considerable theoretical importance. In beginning a study of the principles involved, no more logical starting point seemed to present itself than the direct determination of the solubility, hitherto undetermined, of pure radium sulfate. This determination was carried out in water and in different concentrations of sulfuric acid.

If a solution containing a mixture of radium and barium salts be partially precipitated by the addition of some sulfate, it will be found that the Ra/Ba ratio in the precipitate is the same as in the original solution, and consequently no change of relative concentration results. This precludes the possibility of employing fractional precipitation in separating the two elements, and at once suggests a similarity to the behavior of the isotopic elements, generally recognized as wholly inseparable. We know, of course, that radium and barium are not isotopes, have quite different atomic numbers and are easily separated by other methods such as fractional crystallization of their halide salts. It is, however, important to investi-

[1] Published with permission of the Director of the Bureau of Mines.

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gate how far reaching is this similarity in behavior to isotopic elements, whether it extends, for example, to identical solubility of corresponding salts of radium and barium.

By the conductivity method, Hulett[1] has found the solubility of barium sulfate in water to be 2.3×10^{-6} g. per cc. at 25°. If the inseparability of radium and barium, when precipitated as sulfates, is due to identical solubility, as in the case of isotopes, this value would also hold for radium sulfate. On the other hand the solubility (g. per cc.) of calcium sulfate[2] at 25° is 2.09×10^{-2} and of strontium sulfate[3] 1.5×10^{-4}. If we compare these three known values of solubility with the rising atomic weights of calcium, strontium and barium and make a rough extrapolation to radium (at. wt. 226.0) the solubility of radium sulfate would appear as at least 100 fold less than that of barium sulfate, or of the order of 10^{-8} g. per cc., which would place radium sulfate among the least soluble salts known. Even so low a solubility as this would, however, fail to recover any radium under working conditions. In the work of the U. S. Bureau of Mines[4] in the production of radium from carnotite, 10–15 mg. of radium were precipitated daily together with a one-million fold excess of barium by the addition of excess of sulfuric acid to a solution 4 to 5 thousand liters in volume. Direct determination of Ra showed 6.7×10^{-12} to 1.36×10^{-11} g. per cc. in the filtrate containing about 0.5% sulfuric acid and 2–3% free nitric acid. Attributing the variations observed to some suspended (radium) barium sulfate and taking into account the increase of solubility by the presence of free nitric acid, it is certain that the weight of radium sulfate truly in solution in 1 cc. of filtrate is of the order 10^{-12} g. (It will be later shown that this low value is not due to the repressive effect of excess of sulfuric acid through mass action, but to an entirely different cause.)

It must be admitted then that three values of widely differing orders 10^{-6}, 10^{-8} and 10^{-12} g. per cc. come into consideration as possible ones for the solubility of pure radium sulfate. It is the object of the present paper to decide between these by direct determination.

It might also be mentioned that for the quantitative determination of radium one is fortunate in having the "emanation" method, one of far greater sensitiveness than any possessed for ordinary elements. One is therefore enabled to extend solubility measurements into a region which could not hitherto be reached by the use of direct methods. It will therefore be of some additional interest to note whether the effect of mass action manifests itself at great dilutions.

[1] Hulett, *Z. physik. Chem.*, **37**, 398 (1901).
[2] Hulett and Allen, THIS JOURNAL, **24**, 667 (1902).
[3] Wolfmann, *Oesterr-Ungar. Z. Zuckind.*, **25**, 988 (1896).
[4] Parsons, Moore, Lind and Schaefer, U. S. Bureau of Mines, *Bull.* 104 (1916).

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2. General Procedure.

In order to avoid all possibility of illusive results, it was thought best to approach the equilibrium from both sides to insure a true state of solution. Consequently measurements have been made of solutions prepared both by dissolving radium sulfate, and also by precipitating it from solution.

A possible difficulty was foreseen in the mass-action effect of unavoidable small quantities of sulfate in the water used as solvent, which might produce a marked and uncontrollable depression of a solubility already so low. Happily, it has been found that the solubility in water and in concentrations of sulfuric acid from 0.01 N to 50%, are approximately identical and therefore no especial precautions in this direction are necessary.

It is a well-known fact, frequently employed analytically for the purification of barium sulfate, that it is quite soluble in conc. sulfuric acid. This is also true of radium barium sulfate mixtures[1] and has here been found to be true of pure radium sulfate also. Occasion was therefore taken to extend the investigation to the higher concentrations of sulfuric acid in order to ascertain at what point this enhancement of solubility occurs.

3. Preparation of Pure Radium Sulfate.

As initial substance for the preparation of pure radium sulfate one employs most conveniently 100% radium bromide, which can be readily obtained in this degree of purity by recrystallizing a relatively large quantity of radium (Ba) bromide. Starting with 236.3 mg. of radium (element) in the form of the double bromide containing about 1.25% radium bromide, recrystallization from hydrobromic acid solution[2] was repeated until 150 mg. of radium element were found to have reached 70% purity. This quantity of bromide was then further recrystallized in rapid steps until it was practically certain that the head fraction, now reduced to 35 mg. of element, had reached 100% purity. This salt was then carefully dehydrated at 120° and one portion of 50 mg. (total weight of salt) was quickly weighed on an assay balance, and at once sealed in a glass tube in the usual way for a gamma ray determination of the radium content.[3] 50 mg. radium bromide contain 29.3 mg. radium element, which was exactly the quantity reported by the U. S. Bureau of Standards as contained in the tube on the basis of a gamma ray measurement. After this verification of the purity of the salt, the remaining portion of the same purity (about 5 mg. of element) was divided into two approximately equal portions, one of which was converted into radium sulfate by fuming to dryness several times with pure sulfuric acid.

[1] Schlundt, *J. Phys. Chem.*, **20**, 485–94 (1916).
[2] U. S. Bureau of Mines, *Bull.* **104**, 80–85 (1916).
[3] Rutherford, "Radioactive Substances and their Radiations," 1913, 657–8.

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4. Preparation of the Solutions.

Very small portions of pure radium sulfate were introduced into the following solutions to be saturated with radium sulfate:

I*a*, N — H_2SO_4; I*b*, 0.1 N — H_2SO_4; I*c*, 0.01 N — H_2SO_4; I*d*, specially distilled water.

The quantities of salt introduced, although small, were later found to be several hundred times the quantity required to saturate 10–15 cc. of the solution, which quantity was sealed in long-neck glass flasks.

For attainment of saturation from the precipitation side, the remainder of the pure radium bromide (about 3 mg. of element) was dissolved in 250 cc. of freshly distilled water. Portions of 10 cc. of each were at once diluted with equal volumes so as to furnish 20 cc. of each of the following solutions:

II*a*, 1 N — H_2SO_4; II*b*, 0.1 N H_2SO_4; II*c*, 0.01 N — H_2SO_4; II*d*, 0.1 N — Na_2SO_4.

The quantity of radium contained initially in each of these Class II solutions is 4 to 5 hundred times the amount necessary for saturation. A number of more concentrated solutions, from 10% to 90% sulfuric acid, were also saturated by using portions of the same radium bromide solution.

5. Experimental Procedure.

The small flasks containing the solutions to be saturated with radium sulfate were agitated in a thermostat, electrically heated and regulated, until equilibrium at a fixed temperature was attained. No experiments were made to determine the rate of solution nor of precipitation, but no differences in concentration were to be noted after a few days between the values obtained from the two opposite directions, and the values of Class I solutions were found to have remained constant after eleven months.

Filtration.—One cc. of solution was found to be a suitable quantity for the "emanation" method. Accordingly pipets were carefully calibrated to deliver 1 cc. Preliminary experiments on Class I solutions showed that while it was sometimes possible to remove the supernatant liquid directly, frequently an invisible particle of radium sulfate would be drawn off which would vitiate the result by 75 to 100 fold. To avoid this a filtering tip was ground for each pipet, by means of which the solution was drawn through a layer of cotton (or asbestos fiber for solutions containing more than 45% sulfuric acid) closely packed below a 1 mm. constriction in the tube constituting the tip. A 1-inch layer of cotton was found to be sufficient in general, though an occasional very high result suggested that a particle of solid might sometimes pass through it if not tightly packed.

Adsorption by the filter did not seem greatly to be feared in the short time necessary to draw the solution through, especially as values approximately equal have been occasionally obtained with and without a filter. Nevertheless the following direct test was made: A properly diluted

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solution of radium bromide was prepared without any precipitant being added, and was acidulated with some hydrobromic acid to prevent the precipitation of radium carbonate.

Three 1 cc. portions of this solution were withdrawn in a pipet as follows:

Original, without any cotton; (I), with a fresh layer of cotton; (II), using same layer of cotton immediately after (I).

Two sets of determinations (not comparable with each other) gave the following results for radium (element) left in solution under the three conditions, expressed in g. $\times 10^{-8}$:

Solution.	Original.	I.	II.
First determination.....	1.156	1.010	1.124
Second determination.....	1.333	1.248	1.395

In each case it will be noted that the first portion (I) drawn through cotton is slightly lower than the original, but that the second portion recovers approximately the initial concentration of Ra. The procedure adopted therefore was to discard the first portion drawn through the filter, and at once draw one or two other portions through the same cotton (or asbestos).

Radium Measurements.—The quantity of radium sulfate in solution was determined directly by employing the "emanation" method for the radium itself.[1] The procedure consisted in drawing the solution into the pipet as just described and immediately allowing it to run into a small Pyrex flask (125 cc.) half full of 1–1 nitric acid, which was immediately boiled to expel emanation, sealed a few days for the fresh accumulation of emanation which was boiled off and introduced into the emanation chamber of an "interchangeable" electroscope.[2]

In the cases of the sulfuric acid solutions of higher concentration (above 30%), concentrated sulfuric acid (>95%) was employed as storing solution instead of 1–1 nitric acid to avoid the possibility of any reprecipitation of radium.

6. Experimental Results.

In the following table are given the results for the solubility of radium sulfate, Class I by solution, Classes II and III by precipitation. It will be observed that the values in Classes I and II are practically identical (and also in Class III up to about 50% sulfuric acid indicating that a true state of solution is being dealt with. The absence of repressive effect of excess of sulfuric acid on the solubility of radium sulfate is a very fortunate circumstance, as regards the determination in water (see Introduction) and will also be given further consideration.

[1] Lind, *J. Ind. Eng. Chem.*, 7, 406–10, 1024–29 (1915); U. S. Bureau of Mines, *Bull.* 104, Chap. V.

[2] For details of the "emanation" method see Lind, *Loc. cit.*

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TABLE SHOWING SOLUBILITY OF $RaSO_4$ IN H_2O AND IN SOLUTIONS OF H_2SO_4 AT 25°.

Class I. By Solution of $RaSO_4$.		Class II. By Precipitation of $RaSO_4$.	
Solvent.	Solubility $RaSO_4$ in g. $\times 10^{-8}$ per cc.	Solvent.	Solubility $RaSO_4$ in g. $\times 10^{-8}$ per cc.
N H_2SO_4	2.1	N H_2SO_4	2.3
0.1 N H_2SO_4	2.3	0.1 N H_2SO_4	2.1
0.01 N H_2SO_4	2.0	0.01 N H_2SO_4	2.1
H_2O	2.1	0.1 N Na_2SO_4	(12.0)[1]

Class III. By Precipitation of $RaSO_4$.

Solvent H_2SO_4.	
10%	2.4
15%	2.4
25%	2.3
30%	2.3
Filtered through Asbestos.	
45%	1.9
50%	2.1
55%	3.4
60%	6.3
65%	6.4
70%	(78.8)[2]
80%	(79.2)[2]
90%	(77.6)[2]

To get some idea of the effect of change of temperature on the solubility a few measurements were made at 35° and 45°. In 0.01 N sulfuric acid the solubility at 35° is 3.0×10^{-8} g. per cc., an increase of 50% over the value 2.0×10^{-8} at 25°. In 25% sulfuric acid at 35° the value is 3.3×10^{-8}, an increase of 43.5% over the value 2.3×10^{-8} at 25°, while at 45° in 25% sulfuric acid the value is 5.0×10^{-8} more than double the value at 25° and about 50% higher than at 35°.

7. Discussion of Results.

It is quite evident that the observed solubility of radium sulfate in water, 2.1×10^{-8} g. per cc., agrees with that predicted by the physical-chemical method of extrapolating from the solubilities of calcium, strontium and barium sulfates, and is about 100 times less than that of barium sulfate.

The absence of any effect of sulfuric acid up to 50% on the solubility is notable. The result is not the one to be expected from mass action, but as far as the authors are aware no experimental proof of the applicability of this principle has been made by direct methods for difficultly soluble salts of the bi-bivalent type. Z. Karaoglanow[3] has recently observed that the solubility of barium sulfate also appears to be the same in water as in sulfuric acid up to 0.3 N.

[1] Average of several results showing rather wide deviation.

[2] These three values do not represent saturation, and merely indicate that the solubility exceeded the quantity of Ra available, which was the same in all three cases.

[3] Karaoglanow, *Z. anal. Chem.*, 56, 225–54; *J. Chem. Soc.*, 112, II, 387–8 (1917).

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Since it has been shown that at the higher concentrations of sulfuric acid (above 65%) the solubility of radium sulfate undergoes a marked increase, it might be supposed that at lower concentrations, the solvent effect of the acid is just counterbalancing the repressive effect of sulfate. One experiment with 0.1 N sodium sulfate was made to test this hypothesis, which as will be seen, does not lend it any support. The apparently high solubility of radium sulfate in sodium sulfate solution, suggests either formation of a soluble double salt, or difficult coagulation of radium sulfate in absence of H ion. The former suggestion is supported by the results of Karaoglanow, who found that sodium sulfate as well as potassium sulfate and other salts increased the solubility of barium sulfate. While the latter view, that of difficulty of coagulation, is given support by the variability of the measurements in sodium sulfate, as well as by the recent work of H. B. Weiser,[1] who found Na-ion unfavorable to the coagulation of barium sulfate. The practical result would be the same, that the precipitation and filtration of radium sulfate would be incomplete in the presence of sodium or potassium salts. Since, however, barium is usually present in practice, the authors postpone the further investigation of the effect of electrolytes to a later paper dealing with mixtures of radium and barium.

The *effective* concentration of radium sulfate of the order of 10^{-12} g. per cc., which can be attained as already stated, when a radium barium mixture (1 to 1,000,000) is precipitated by an excess of sulfuric of 0.5% concentration, is not to be explained by the mass action effect of excess of precipitant, but by a new and yet imperfectly understood principle of inseparability of certain elements like radium and barium by precipitation. The difference of 100-fold solubility between radium sulfate and barium sulfate shows that the precipitation is in direct controversion of mass action. A fuller discussion will be found in a later paper under the title of "Pseudo-isotopy," which term one of the authors proposed at the Kansas City meeting, (April 7, 1917) of the Amer. Chem. Soc.[2] At present suffice it to say that in a solution with not too great excess of sulfuric acid, the solubility of barium sulfate is 2.3×10^{-6} and the effective solubility of radium sulfate would be this value multiplied by the Ra/Ba ratio obtaining in the solution before precipitation. In case this ratio were 1/1,000,000 its effective solubility would then be of the order 10^{-12} g. per cc., which has actually been found by repeated experiments under these conditions, as stated in the Introduction.

Summary.

1. The solubility of pure radium sulfate in 1 cc. of water at 25° is 2.1×10^{-8} g., about 100-fold less than that of barium sulfate.

2. The solubility at 25° of pure radium sulfate in sulfuric acid solutions

[1] H. B. Weiser, *J. phys. Chem.*, 21, 314–35 (1917).

[2] *Science*, 46, 170 (1917).

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is identical with that in water from 0.01 N up to 50% acid. The same values were obtained either by dissolving or precipitating the radium sulfate indicating a true state of solution.

3. The value found is that predicted from comparison with the decreasing solubilities of calcium, strontium and barium sulfates.

4. Excess of sulfuric acid does not have a repressive effect on the solubility of radium sulfate.

5. On increasing the concentration of sulfuric acid above 65%, a marked rise in solubility of radium sulfate takes place, and it is more than 12 times as soluble in 70% as in 65% acid.

6. An explanation is given of the "effective solubility" of radium sulfate (when precipitated together with large excess of barium) which is found to be far below the actual solubility of radium sulfate.

7. The solubility of radium sulfate in sulfuric acid solutions up to 25% acid is about 50% higher at 35° than at 25° and again increases about 50% in the temperature interval 35° to 45°.

U. S. BUREAU OF MINES,
GOLDEN, COLORADO.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

EQUILIBRIA INVOLVING CYANOGEN IODIDE; THE FREE ENERGY OF FORMATION OF CYANOGEN.

BY GILBERT N. LEWIS AND DONALD B. KEYES.

Received December 12, 1917.

While there is doubtless an equilibrium between carbon, nitrogen and cyanogen at the temperature of the electric arc, it has not hitherto been found practicable to determine the free energy of formation of cyanogen through a study of this simple equilibrium. It is, however, possible, when the free energy of formation of hydrocyanic acid is known, to obtain that of cyanogen by the aid of two reversible reactions. The study of the equilibrium in these reactions will form the subject of this paper.

The Dissociation of Cyanogen Iodide.

The two reactions to which we have referred both involve the interesting substance cyanogen iodide (or as it might perhaps better be called, iodine cyanide). This is a white substance which, on moderate heating, decomposes readily according to the reaction

$$2\,CNI = (CN)_2 + I_2.$$

When the substance is heated in a closed tube the dissociation evidently occurs until a definite equilibrium is established, and solid cyanogen iodide remains in the presence of its own vapor, gaseous iodine, and cyanogen. Since the vapor of cyanogen iodide dissociates without change of volume, and since the reaction is evidently too rapid to permit a determination of

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the equilibrium by a sudden cooling of the vapors, no ordinary means of determining the degree of dissociation is available. Since, however, cyanogen iodide and cyanogen are both colorless, it seemed feasible to determine the concentration of iodine vapor colorimetrically.[1]

For this purpose two similar tubes of quartz, each closed at the ends by polished quartz windows, were employed. These are shown as A and C in Fig. 1, where the tube A is connected by a quartz side tube to the bulb B, containing an excess of solid cyanogen iodide. The side tube leading from C emerges from the air thermostat containing the tubes and leads to the bulb D filled with solid iodine and immersed in a small oil thermostat H. The air thermostat was provided with the necessary stirrer, heater and regulator, not shown in the diagram, and with glass windows, E and F, through which the light from a frosted incandescent lamp could pass through the tubes A and C into the optical parts of a colorimeter placed above the window E.

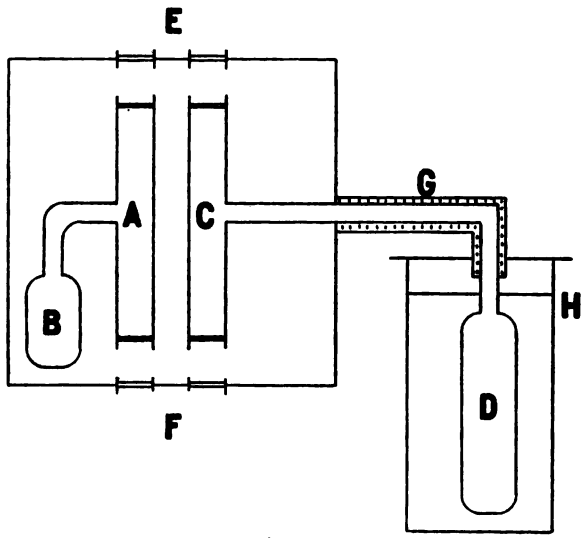

Fig. 1.

When the air thermostat is heated to the desired temperature, the oil thermostat may be kept at a lower temperature such that the intensity of color of the pure iodine in C just matches that of the iodine in the mixed vapor in A. In order to avoid a condensation of the iodine vapor between the two thermostats, this portion of the connecting tube was heated by a coil of wire G. Some trouble was caused at first by the condensation of the solids upon the quartz windows; this was subsequently avoided by the aid of small auxiliary heating coils placed near these windows, and not shown in the figure. These coils were removed shortly before the final equilibrium was established. The tubes containing iodine and cyanogen iodide were completely exhausted of air before the experiments began.

The first experiments were disappointing. When the air thermostat was kept at a constant temperature, in the neighborhood of 100°, the in-

[1] The apparatus was largely constructed by Dr. R. L. Sebastian, to whom we are also indebted for some preliminary measurements in this reaction and in the one discussed in the following section.

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tensity of color in the cyanogen iodide tube increased slowly until, at the end of several hours, equilibrium seemed to be established; but, on further standing, the color once more deepened and continued to do so without apparent limit. This phenomenon we attributed to the removal of cyanogen by the deposition of para-cyanogen upon the walls of the tube. This conversion of cyanogen into para-cyanogen is markedly autocatalytic, but it was found that with the exercise of reasonable precautions, such as keeping the tube free from dust and avoiding all cyanogen iodide at the point where the tube was sealed off after filling, it was possible to reach and maintain equilibrium for an hour or two, before the formation of para-cyanogen set in.

When the dissociation had reached the constant value, the temperature of the oil thermostat was varied until a color match was procured (a slight correction being made for lack of exact equality in the length of the two quartz tubes). Since the partial pressure of iodine is now the same in both tubes it is only necessary to know the vapor pressure of solid iodine at the temperature of the oil bath, in order to find its pressure over the cyanogen iodide; and this vapor pressure of solid iodine can be obtained at once from a plot in which we incorporated the data of Baxter, Hickey and Holmes,[1] and of Ramsay and Young.[2]

Four measurements were made, each with a complete refilling of the apparatus in order to avoid the accumulation of para-cyanogen. The results are given in Table I. The first column shows the temperature of the air bath, and the second gives the values of p, the partial pressure of the iodine expressed in mm. Since one mol of cyanogen is produced for each mol of iodine the two partial pressures are the same, and the product of these two, expressed in atmospheres, $K = p^2/760^2$, is the equilibrium constant for the reaction

$$2\ CNI(s.) = (CN)_2(g.) + I_2(g.).$$

TABLE I.

t.	p.	K.
90.0	3.42	2.00×10^{-6}
110.0	21.08	7.76×10^{-4}
116.5	33.1	1.91×10^{-3}
123.0	56.7	5.63×10^{-3}

The values of log K plotted against the reciprocal of the absolute temperature fall very nearly upon a straight line which, extrapolated to 25°, gives log $K_{298} = -10.95$. From the slope of this line we may find the heat absorbed in the reaction $\Delta H = 48000$ cals. Berthelot made two determinations of this heat.[3] From the first $\Delta H = 41800$; from the second

[1] Baxter, Hickey and Holmes, THIS JOURNAL, 29, 127 (1907).

[2] Ramsay and Young, *J. Chem. Soc.*, 49, 453 (1886).

[3] Berthelot, *Ann. chim. phys.*, 5, 433 (1875); 23, 252 (1881).

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$\Delta H = 9100$. Each of these determinations was based upon a large number of separate reactions, and in the absence of any more direct determinations we shall adopt the value calculated from equilibrium measurements, and also therefore the value of log K_{298} given above.

We may now calculate the free energy of the reaction from the equation $\Delta F^\circ_{298} = -1364.9 \log K_{298}$; or, substituting the given value

$$2CNI(s.) = (CN)_2(g.) + I_2(g.);\ \Delta F^\circ_{298} = 14950. \qquad (1)$$

Equilibrium in the Reaction between Cyanogen Iodide and Hydriodic Acid.

In order to determine the free energy of formation of cyanogen iodide we have investigated a reaction which was shown to be reversible by von Meyer,[1] namely,

$$CNI + HI \rightleftharpoons HCN + I_2.$$

If a mixture of solid cyanogen iodide and iodine is treated with a dilute aqueous solution of hydriodic acid, prepared according to the method of Bray and MacKay,[2] equilibrium is readily established, but there are numerous difficulties in the determination of the composition of the equilibrium mixture. We have attempted to measure the vapor pressure of hydrogen cyanide over the mixture and to determine the concentration of hydrogen ion and iodide ion in solution.

For this purpose the mixture was placed in a bubbler of simple construction so designed as to permit the gas which passes through to remain for some time in contact with the solution, while the pressure throughout the apparatus is kept essentially constant. In order to avoid errors due to oxidation of the hydriodic acid, pure nitrogen, prepared from ammonium nitrite, was passed through the bubbler. This nitrogen was stored over water which was protected from the oxygen of the air by a tube containing moist phosphorus. The measurements were made in a thermostat at 25°. Each experiment lasted from twelve to fifteen hours, about two liters of nitrogen passing through the apparatus. From the bubbler this gas was led through glass wool to catch any spray and thence out of the thermostat into another bubbler containing 0.1 M sodium hydroxide to absorb the vapor of hydrogen cyanide. This solution was later slightly acidified and treated with silver nitrate, the silver cyanide being filtered and weighed.

In order to obtain the concentration in the aqueous phase from the partial pressure of the HCN the distribution constant must be known. A rough determination of this constant, which will suffice for our present purpose, was made with the apparatus just described. If P is the pressure in atmospheres and m the concentration in mols per thousand grams of water, $K = P/m = 0.096$. Hence,

$$HCN(aq.) = HCN(g.);\ \Delta F^\circ_{298} = 1390. \qquad (2)$$

[1] Von Meyer, *J. prakt. Chem.*, 36, 292 (1887).

[2] This Journal, 32, 1195 (1910).

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Returning to the main reaction which we may write in the form CNI(s.) + H^+ + I^- = HCN(g.) + 2I(s.), the results of five equilibrium measurements are given in Table II. The first column gives the molal concentration of the original solution of hydriodic acid, and the second the partial pressure of hydrogen cyanide.

Owing to our ignorance of the amount of cyanogen iodide dissolved as such and of the products of its hydrolysis, the determination of the concentration of H^+ and I^- is far from simple. If we find the concentration of hydrogen cyanide produced in the reaction by dividing its partial pressure by the distribution constant, and if this concentration is subtracted from the original concentration of hydrogen iodide the result should equal the concentration of hydrogen iodide and hydrogen tri-iodide remaining, provided that no other reaction occurs except the one under consideration. If the concentration so obtained is multiplied by the degree of dissociation[1] we obtain the concentration of H^+ given in Col. 3.

TABLE II.

HI(orig.).	*P*(HCN).	H^+.	I^-.	*K*.
0.0296	0.00115	0.0161	0.0065	11.0
0.1038	0.00605	0.0361	0.0144	11.6
0.1020	0.00675	0.0285	0.0118	20.2
0.0677	0.00360	0.0268	0.0100	13.4
0.0764	0.00471	0.0246	0.0106	18.0

If we could be sure that no anions were present in solution except I^- and I_3^-, the concentration of I^- could readily be determined from that of H^+ by means of data at hand on the equilibrium between iodine, iodide, and tri-iodide. This seemed, however, an unsafe assumption, and numerous methods were considered, all of which failed owing, we believe, to the peculiar reactivity of the dissolved cyanogen iodide. Finally, after the first two experiments were completed, a method was devised which seemed capable of giving definite information as to the composition of the solution.

The reaction vessel was reconstructed so that after attainment of equilibrium the solution could be forced, without change of composition or temperature, into an electrode vessel of the pipet type containing a platinum electrode. This, stationed in a thermostat at 25°, could be connected to other electrode vessels of the same type containing solid iodine and hydrogen iodide of several known concentrations. In this way it was possible to find a definite concentration of hydrogen iodide in the second half-cell such that the e. m. f. of the combination became zero. Since both solutions are saturated with solid iodine this would mean, if no other substance besides hydrogen iodide and hydrogen tri-iodide were present, an identity

[1] If we assume the corrected degree of dissociation in the mixture of hydrogen iodide and hydrogen tri-iodide to be the same as that of hydrogen chloride we may take for the degree of dissociation 0.91 in the first experiment, 0.88 in the second, and 0.89 in the remainder.

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of the two solutions. As a matter of fact, however, the concentration of acid in the comparison electrode proved to be less in each case than that which was calculated by the above method for the concentration of acid left in the equilibrium chamber, being 81.3% of the latter in the third experiment, 72.5% in the fourth, and 84.7% in the fifth, average 79.5%. Since the e. m. f. depends only upon the concentration of I^-, we are unable to explain the difference, except upon the assumption that cyanogen iodide, like iodine, forms a complex ion with I^-, thus diminishing the concentration of the latter. We shall assume therefore that in the first two experiments where the direct measurements were not made the sum of the concentrations of I^- and I_3^- is smaller than the concentration of H^+ in the ratio just given for the last three experiments namely 0.795. Of this concentration about half is due to I^- and one-half to I_3^-. According to the measurements of Bray and MacKay[1] the ratio of iodide to tri-iodide is 1.03 at the highest of our concentrations at 1.05 at the lowest. Using these data we obtain the concentration I^- given in Col. 4 of Table II.

The equilibrium constant as determined by our equation is equal to the pressure of hydrogen cyanide divided by the product of the concentrations of H^+ and I^-, $K = [HCN]/(H^+)(I^-)$. The values of K so calculated are given in the last column of Table II. The last experiment can be given little weight owing to the fact that in this case only about one-third as much nitrogen was passed through the bubbler as in the other cases, and the determination of the presence of hydrogen cyanide is therefore uncertain.

Unquestionably the interesting reactions involved in this equilibrium are worthy of a far more careful investigation than we have been able to make at the present time, but the results are adequate for our present purpose and we shall take as a sort of a weighted mean $K = 13$. Hence we find,

$$CNI(s.) + H^+ + I^- = HCN(g.) + 2I(s.); \quad \Delta F^\circ_{298} = -1520. \qquad (3)$$

Combining this with Equation 2 gives

$$CNI(s.) + H^+ + I^- = HCN(aq.) + 2I(s.); \quad \Delta F^\circ_{298} = -2910. \qquad (4)$$

We may combine with this equation the following:

$$HCN(aq.) = {}^1/_2H_2 + C_G + {}^1/_2N_2; \quad \Delta F^\circ_{298} = -23421,^2$$

$$I(s.) = I^- + \oplus; \quad \Delta F^\circ_{298} = -12304,^3$$

$${}^1/_2H_2 + \oplus = H^+; \quad \Delta F^\circ_{298} = 0.^4$$

Whence,

$$C_G + {}^1/_2N_2 + I\ (s.) = CNI(s.); \quad \Delta F^\circ_{298} = 38635. \qquad (5)$$

[1] Bray and MacKay, THIS JOURNAL, 32, 914 (1910).
[2] Lewis and Brighton, *Ibid.*, 40, 482 (1918).
[3] Lewis and Randall, *Ibid.*, 36, 2259 (1914).
[4] Lewis and Randall, *Ibid.*, 36, 1969 (1914).

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If we combine Equations 1 and 5 of this paper with the equation for the free energy of iodine vapor,[1]

$$2I(s.) = I_2(g.);\ \Delta F^\circ_{298} = -4640$$

we obtain finally the free energy of formation of cyanogen gas,

$$2C_G + N_2 = (CN)_2(g.);\ \Delta F^\circ_{298} = 87580. \qquad (6)$$

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI.]

REACTIONS IN NON-AQUEOUS SOLVENTS. II. THE ACTION OF CHROMYL CHLORIDE UPON PHOSPHORUS HALIDES.

BY HARRY SHIPLEY FRY AND JOSEPH L. DONNELLY.

Received December 18, 1917.

In the first paper of this series[2] it was shown that the dangerously explosive interaction between chromyl chloride and the phosphorus trihalides could be controlled and studied quantitatively by conducting the reactions in anhydrous carbon tetrachloride solutions. Equimolar solutions of chromyl chloride and phosphorus trichloride and tribromide were found to interact in the ratio of two volumes of the former to three volumes of the latter, *i. e.*, $2CrO_2Cl_2 : 3PX_3$(X = Cl or Br), yielding new compounds of the formulas $CrOCl.POX_3$ according to the general equation

$$2CrO_2Cl_2 + 3PX_3 \longrightarrow 2CrOCl.POX_3 + PX_3Cl_2.$$

The determination of these ratios by volumetric methods was rendered possible through the use of acetyl bromide as an indicator for the detection of minute traces of chromyl chloride, the end point of the reaction depending upon the formation of the unstable but intensely colored (violet-red) chromyl bromide.[3]

This paper presents briefly the results of a further quantitative study of the action of chromyl chloride upon the following phosphorus halides: (A) Triiodide, (B) Pentachloride, (C) Pentabromide, and (D) Diiodide.

A. Interaction of Chromyl Chloride and Phosphorus Triiodide.

A volumetric study of the interaction of 0.2 *M* solutions of chromyl chloride and phosphorus triiodide in anhydrous carbon tetrachloride using acetyl bromide as an indicator (method described in Part I, Section A, *loc. cit.*) could not be effected because the slightly violet-red color of the phosphorus triiodide solution, due to inevitable traces of free iodine, invariably obscured the end point of the reaction. However, equimolar (0.2 *M*) solutions of chromyl chloride and phosphorus triiodide interacted exothermally, and instantaneously, yielding a voluminous dark brown precipitate, which, after being filtered, and repeatedly washed with carbon tetrachloride

[1] Lewis and Randall, THIS JOURNAL, 36, 2259 (1914).

[2] Fry and Donnelly, *Ibid.*, 38, 1923 (1916).

[3] Fry, *Ibid.*, 33, 697 (1911).

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and dried in a current of air free from moisture and carbon dioxide, was found to be a purple-red powder, too deliquescent and unstable for microscopic examination. The addition of a few drops of water to the compound effected violent decomposition with liberation of clouds of iodine vapor. Boiling with an excess of water gave a solution containing chromic, phosphate, chloride and bromide ions. This facilitated the quantitative analysis of the compound for the chromium and halogen content.

Determination of Chromium.—Weighed samples of the compound were dissolved in water. Boiling volatilized the free iodine. Cr^{+++} was oxidized to CrO_4^{--} by the addition of sodium peroxide. After successive treatments with sodium peroxide and dilute sulfuric acid, the percentage of chromium was determined by titration with 0.1 *N* ferrous ammonium sulfate solution, with the following results:

Compound (g.).	0.1 *N* ferrous soln. cc.	% Cr found.
0.2486	13.00	9.05
0.5984	31.15	9.02

It was naturally supposed that phosphorus triiodide and chromyl chloride would yield a compound of the formula $CrOCl.POI_3$, just as phosphorus trichloride and tribromide had previously yielded $CrOCl.POCl_3$ and $CrOCl.POBr_3$, respectively. This, however, was not the case since the percentage of chromium in the anticipated compound $CrOCl.POI_3$, 9.78 is not in agreement with the above values for chromium.

Determination of Halogens.—Since treatment of the compound in question with water involved the liberation of iodine and hydrogen halides, the following method was adopted: Weighed samples were placed in test tubes of 50 cc. capacity and covered with 10 cc. of carbon tetrachloride, which, in turn, was covered with 35 cc. of water. The tubes were securely stoppered and shaken. This procedure yielded a carbon tetrachloride solution of the liberated iodine and an aqueous solution of chlorides and iodides which were subsequently precipitated and weighed as mixed silver halides, $(AgCl)_x(AgI)_y$. Since the theoretical halogen content for the compound in question was not known, a value in the form of a factor, based upon the ratio of the quantity of the mixed halides found to the quantity of the compound taken for analysis, was determined as follows:

Compound (g.).	(AgCl)(AgBr) (g.).	Factor.
0.1098	0.1475	1.343
0.2440	0.3262	1.336

As the interaction between chromyl chloride and phosphorus triiodide did not yield the anticipated compound $CrOCl.POI_3$ the substance obtained was assumed to be an addition compound of the formula $CrO_2Cl_2.PI_3$, which would be decomposed by water according to the equation

$$2CrO_2Cl_2.PI_3 + 4H_2O \longrightarrow 4HCl + 4HI + 2CrPO_4 + I_2.$$

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According to this equation, $CrO_2Cl_2.PI_3$ should yield $2AgCl + 2AgBr$ when the compound is decomposed by water and the resulting solution is treated with silver nitrate as described above. Accordingly, the theoretical ratio or factor should be $(CrO_2Cl_2.PI_3) : (AgCl)_2(AgI)_2 = 1.334$. This factor is substantiated by the experimentally determined factors given above. Moreover, the percentage of chromium in the addition compound $CrO_2Cl_2.PI_3$, namely 9.18, is checked by the percentages found: 9.05 and 9.02.

In summarizing Part A, it should be noted that while phosphorus trichloride and tribromide interact with chromyl chloride in anhydrous carbon tetrachloride according to the equation

$$2CrO_2Cl_2 + 3PX_3 \longrightarrow 2CrOCl.POX_3 + PX_3Cl_2,$$

which is an *oxidation-reduction reaction*, the behavior of phosphorus triiodide is abnormal in that it forms an *addition compound* according to the equation

$$CrO_2Cl_2 + PI_3 \longrightarrow CrO_2Cl_2.PI_3.$$

B. Interaction of Chromyl Chloride and Phosphorus Pentachloride.

When equal volumes of 0.1 *M* solutions of chromyl chloride and phosphorus pentachloride, in anhydrous carbon tetrachloride, are mixed, a brown gelatinous precipitate is formed. The reaction is exothermal but proceeds so slowly that a titrimetric study was impossible. After the reaction mixture had stood for an hour, the precipitate was filtered, repeatedly washed with carbon tetrachloride, and dried in a current of air free from moisture and carbon dioxide. The yellow-red powder thus obtained readily decomposes in the air evolving hydrogen chloride. It is vigorously decomposed by water yielding a solution containing chromic, phosphate, and chloride ions. The compound was analyzed for its chromium and chlorine contents by the methods outlined in the preceding Section A. The results of the analyses clearly indicate that an addition compound was formed according to the equation

$$CrO_2Cl_2 + PCl_5 \longrightarrow CrO_2Cl_2.PCl_5.$$

Data for Chromium Determinations:

Compound (g.).	0.1 *N* ferrous soln. (cc.).	% Cr found.	% Cr theory.
0.1487	12.05	14.04	14.08
0.2086	17.10	14.20	...

Data for Chlorine Determinations:

Compound (g.).	AgCl (g.).	% Cl found.	% Cl theory.
0.1131	0.3121	68.27	68.34
0.1470	0.4053	68.21	...

C. Interaction of Chromyl Chloride and Phosphorus Pentabromide.

Equimolar quantities of chromyl chloride and phosphorus pentabromide in carbon tetrachloride solution react exothermally yielding a gray, gelatinous precipitate which, when dried according to previously described methods, was found to be a dark purple powder, readily decomposed by

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atmospheric moisture with the evolution of fumes of hydrochloric and hydrobromic acids. Treatment with water gave a solution containing chromic, phosphate, chloride and bromide ions.

By analogy to the preceding reaction (B) with phosphorus pentachloride, the pentabromide should have formed a molecular compound of the formula $CrO_2Cl_2.PBr_5$, but repeated analyses of the product for chromium and halogen contents did not confirm the analogy. Repetitions of the interaction with varying concentrations of chromyl chloride and phosphorus pentabromide failed to yield a product of constant composition.

This anomaly may be explained by the fact that phosphorus pentabromide in carbon tetrachloride solution is partially dissociated and, consequently, embodies the reaction components of the equilibrium mixture

$$PBr_5 \rightleftharpoons PBr_3 + Br_2.$$

Phosphorus tribromide, as previously described,[1] reacts readily with chromyl chloride to give the compound $CrOCl.POBr_3$; and a part, at least, of the phosphorus pentabromide would lend itself, presumably, to the formation of an addition compound $CrO_2Cl_2.PBr_5$, the analog of the compound $CrO_2Cl_2.PCl_5$ prepared in Section B. From this point of view, the product of the interaction of chromyl chloride and phosphorus pentabromide is a variable mixture of two compounds, $CrOCl.POBr_3$ and $CrO_2Cl_2.PBr_5$, which would not give concordant analyses for a definite addition compound.

D. Interaction of Chromyl Chloride and Phosphorus Diiodide.

The reaction between 0.1 *M* solutions of chromyl chloride and phosphorus diiodide (P_2I_4) is highly exothermal with instantaneous precipitation of a compound which, recovered by the usual method, was brown in color and very unstable in moist air. Iodine is freely evolved upon the addition of water, and subsequent boiling gives a solution containing chromic, chloride and iodide ions.

The results of the analyses for chromium indicate the formation of an addition compound according to the equation

$$2CrO_2Cl_2 + P_2I_4 \longrightarrow (CrO_2Cl_2)_2.P_2I_4.$$

Compound (g.).	0.1 *N* ferrous soln. (cc.).	% Cr found.	% Cr theory.
0.2005	13.90	12.01	11.82
0.1805	12.45	11.95	...

In the determination of the halogen content, a method was designed to precipitate all of the halogen in the compound as mixed silver halides in the ratio demanded by the assumed formula, namely 4 (AgCl.AgBr) : $(CrO_2Cl_2)_2.P_2I_4$ = 1.719.

Weighed samples were placed in test tubes of 50 cc. capacity and covered with 10 cc. of carbon tetrachloride to which was added a supernatant layer of 35 cc. of sodium thiosulfate solution. The tubes were then

[1] Fry and Donnelly, THIS JOURNAL, 38, 1926 (1916).

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securely stoppered and shaken, thus bringing the samples into contact with the aqueous solution. In this manner the liberated iodine, as well as the remainder of the halogen in the compound, was converted into sodium halides. Boiling the solution with dilute nitric acid, and the subsequent addition of an excess of silver nitrate solution precipitated all of the halogen in the compound as mixed silver chloride and iodide. The results of the determinations check the theoretical factor, noted above, and confirm the formula $(CrO_2Cl_2)_2.P_2I_4$.

Compound (g.).	AgCl.AgI (g.).	Factor, found.	Factor, theory.
0.1872	0.3468	1.715	1.719
0.1169	0.2004	1.714	...

Summary.

The extended study of the interaction of chromyl chloride and phosphorus halides in anhydrous carbon tetrachloride solutions reveals the following facts:

1. While the interaction between chromyl chloride and phosphorus trichloride, or tribromide, is an *oxidation-reduction reaction* conforming to the equation

$$2CrO_2Cl_2 + 3PX_3 \longrightarrow 2CrOCl.POX_3 + PX_3Cl_2 (X = Cl \text{ or } Br),$$

the interaction with phosphorus triiodide unexpectedly gave an *addition compound* of the formula $CrO_2Cl_2.PI_3$.

2. The interaction with phosphorus pentachloride likewise resulted in the formation of an addition compound, $CrO_2Cl_2.PCl_5$.

3. The interaction with phosphorus pentabromide gave no definite compound but, presumably, a mixture of compounds, $CrOCl.POBr_3$ and $CrO_2Cl_2.PBr_5$.

4. The interaction with phosphorus diiodide gave a compound corresponding in composition to the formula $(CrO_2Cl_2)_2.P_2I_4$, or, more briefly, $CrO_2Cl_2.PI_2$. This substance is similar in composition and properties to the compound $CrO_2Cl_2.PI_3$ noted in (1).

5. None of these compounds has been prepared before. Their constitution is unknown, and they do not lend themselves to classification according to the Werner coördination formulas.

CINCINNATI, O.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

THE OXIDIZING POWER OF CYANATES AND THE FREE ENERGY OF FORMATION OF CYANIDES.

BY GILBERT N. LEWIS AND THOMAS B. BRIGHTON.

Received December 20, 1917.

In attacking the difficult problem of free energy changes in organic reactions it has seemed at the outset necessary to determine the free energy of formation, through reversible synthesis from the elements of several

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fundamental organic substances. Two such substances, urea and formic acid, have already been reversibly synthesized.[1]

Hydrocyanic acid, which enters into so many different types of reactions, is an especially important point of departure for organic preparations. Since its reversible formation from the elements is known to occur at very high temperatures, it would seem that a study of this reaction would lead most directly to a knowledge of its free energy of formation. Indeed von Wartenberg[2] has determined the amount of hydrogen cyanide obtained by passing a mixture of hydrogen and nitrogen past a rod of carbon kept at 1908° to 2148° A., but the difficulty of measuring these high temperatures, the fact that the yield of hydrogen cyanide depended upon the rate of flow, and the possibility of a reversal of the reaction before the gas was cooled, make it uncertain whether the yield which he obtained represented true equilibrium.

By an extremely indirect method, but nevertheless through a series of reactions, each of which lends itself to an exact study of equilibrium at moderate temperatures, we have obtained data from which the free energy of formation of hydrocyanic acid may be calculated. From the equilibrium between KCNO, CO, KCN and CO_2, which will be discussed in the following section, and from experiments which will also be described in this paper permitting the calculation of the free energy of solution of potassium cyanate and potassium cyanide, we calculate the equilibrium in the reaction

$$CNO^- + CO(g.) = CN^- + CO_2(g.).$$

The free energy of formation of CNO^- being known from the work of Lewis and Burrows, and that of CO and CO_2 from the calculations of Lewis and Randall on the free energy of the carbon compounds,[3] the free energy of formation of cyanide ion follows directly. From this the free energy of formation of hydrogen cyanide may be immediately obtained since its dissociation constant is known.

The Equilibrium between KCNO, KCN, CO and CO_2.

It is known that fused cyanide is readily oxidized by the air to cyanate. It seemed likely therefore that, by the use of a milder oxidizing agent, a reaction leading to a definite equilibrium would occur. Eiloart[4] found that fused cyanide was oxidized by carbon dioxide, and a few experiments sufficed to show us that fused cyanate is in part reduced by carbon monoxide.[5]

[1] Lewis and Burrows, This Journal, 34, 1515 (1912); Branch, *Ibid.*, 37, 2316 (1916).

[2] Von Wartenberg, *Z. anorg. Chem.*, 52, 299 (1907).

[3] Lewis and Randall, This Journal, 37, 458 (1915).

[4] Eiloart, *Chem. News*, 54, 88 (1886).

[5] The preliminary study of the reversibility of this reaction was made in this laboratory by Dr. H. Ehrenberg.

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Before proceeding to the study of the equilibrium in this reaction it was decided, for the sake of convenience in the later calculations, to use a fused mixture of potassium cyanide and potassium cyanate of the same composition as that which is in equilibrium with the two solid salts at their eutectic point. The composition of this eutectic mixture was found by mixing the salts in trial proportions. Eleven of these mixtures were made up, 100% KCNO, 90% KCNO, ..., 10% KCNO, 100% KCN, by weight. The salts were first fused to secure thorough mixing and then, after cooling, were put into a fused nitrate bath which was heated and allowed to cool until the least fusible mixtures were eliminated. It was soon found that the eutectic mixture would contain between 10% and 20% KCN; more tubes were then prepared containing 11, 12, 13, ..., 20% KCN. The three most easily fusible contained 14, 15 and 16% KCN. Then a small Dewar tube made of Jena glass was used, and carefully weighed mixtures containing 14, 15 and 16% KCN were fused. Each was allowed to cool very slowly, and when partly solidified the liquid was drawn through a plug of glass wool into a small tube. This liquid was then allowed to solidify, weighed, and analyzed for potassium cyanide by titrating with standard silver nitrate solution. The sample from the 14% mixture contained 14.58% KCN, from the 15% mixture in two experiments 14.55% and 14.71%, from the 16% mixture 14.61% and 14.63%. The eutectic mixture contains, therefore, 14.6% KCN and this mixture was used in all the following work. The eutectic temperature was found to be 282° C.[1]

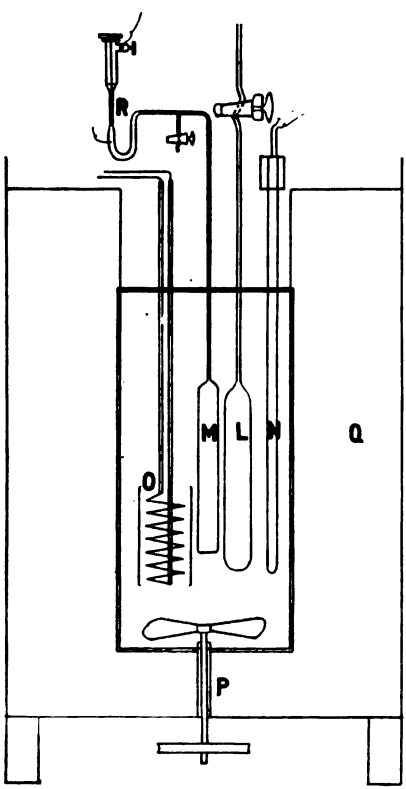

Fig. 1.

The experiments about to be described were made in the apparatus[2] shown in Fig. 1. The air thermostat was composed of a 9-inch iron pipe, wrapped with nichrome wire for heating, and enclosed in alundun cement.

[1] It seemed highly improbable that KCN and KCNO would form solid solutions, and there was nothing in the experiments described above which would indicate the existence of such solutions.

[2] This apparatus was in part designed by Professor Randall for another purpose.

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It was further insulated by a 6-inch layer of magnesia asbestos mixture, Q, this packing being held in place by a galvanized iron casing. Through the bottom of the bath, which was made of soapstone, ran a shaft, P, leading to a fan of monel metal, with a bearing of graphite. The top of the bath was made of two pieces of transite board cut to fit the glass tubes leading to the reaction vessel, and covered with six inches of loose asbestos.

Through this top was also led a silver tube connected to a silver bulb, M, which, operating as an air thermometer, communicated with the temperature regulator R. It operated an auxiliary heater, O, of nichrome wire within the bath. This heater was surrounded by a shield of monel metal to protect the regulator and reaction vessel from direct radiation. Owing to the fact that the equilibrium under consideration changes only slightly with the temperature, it was sufficient to keep the temperature constant within two or three degrees. The temperature was read by means of a resistance thermometer, N.

The reaction vessel L was a bulb of Jena glass 7 inches long and 1.5 inches in diameter. A small Jena glass tube led from this bulb out of the bath. In order to diminish the volume of gas of unknown temperature this tube was nearly filled by a rod of quartz. Outside the bath the Jena glass tube was connected by means of de Khotinski cement to ordinary glass tubing leading to the vacuum pump, the carbon dioxide supply, and the analytical apparatus.

The cyanide and cyanate used contained only a small trace of carbonate and were free from any appreciable amount of any other impurity except water. Since both substances react with water at high temperatures, they were dried as far as possible in a vacuum desiccator and then were brought into the reaction vessel with as little exposure to the air as possible. The vessel was then exhausted and heated very gradually while attached to the pump. After several hours' heating *in vacuo* dry carbon dioxide was allowed to enter at atmospheric pressure and to remain until equilibrium was established.

It was found possible to introduce the salts in such quantities as to give just the eutectic composition as shown by analysis. Potassium cyanide may be readily determined in the presence of cyanate by titrating with silver nitrate and a few drops of iodide solution as indicator, but the determination of cyanate is attended with greater difficulties. We first attempted to analyze for cyanate by acidifying and converting to ammonium ion according to the reaction

$$CNO^- + H_2O + 2H^+ = CO_2 + NH_4^+.$$

However, when acid is added to a cyanate solution, a gas of pungent odor escapes with the carbon dioxide. Even when the cyanate was placed in one arm of an H tube and dilute acid in the other, and the tube sealed, shaken and kept at 100° for an hour, the results obtained, either by de-

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termining the ammonia produced, or the amount of acid neutralized, did not correspond to more than 92% of the cyanate used.

Satisfactory results were finally obtained by treating with an excess of silver nitrate of known concentration, diluting to a known volume, filtering off an aliquot portion from the silver cyanate and titrating the excess silver nitrate with potassium thiocyanate. The silver cyanate is sufficiently insoluble in the presence of an excess of silver ion to prevent appreciable error. Error will be caused, however, if the solution of cyanate is allowed to stand long enough for decomposition according to the reaction $CNO^- + 2H_2O = HCO_3^- + NH_3$. When cyanide is also present it must first be determined separately.

Since in the reaction one mol of carbon monoxide is formed from one mol of carbon dioxide, small portions of the gas in the reaction chamber could be withdrawn for analysis from time to time without disturbing the equilibrium. The gas to be analyzed was transferred by a mercury pump to the measuring pipet, brought to known concentration, and the pressure measured. The gas was then pumped through a concentrated solution and then over moist sticks of potassium hydroxide. After sufficient time for the complete absorption of carbon dioxide, the gas was pumped back over phosphorus pentoxide into the measuring pipet where, at the original volume, its pressure was again measured. In the first experiments this process was repeated in order to ensure the complete absorption of carbon dioxide. In a number of cases the residual gas was exploded with air and, by absorption of the resulting carbon dioxide, was shown to be pure carbon monoxide. In no case was there found a measurable amount of any other gas.

The attainment of equilibrium required less than two days at 550° C., from four to six days at 500°, and in the three determinations at 450° equilibrium appeared to be established in about a month; but a comparison of the results with those at the two higher temperatures seemed to indicate that even in that period equilibrium was not fully established. At 500°, however, there can be no question that true equilibrium was established, since it was approached several times from higher as well as from lower temperatures with identical results. Table I gives the absolute tem-

TABLE I.

T.	K.	T.	K.
721	(1.86)	781	1.99
724	(1.92)	816	2.22
770	1.98	823	2.28
774	1.98	840	2.35
776	1.97	840	2.29
778	2.03	841	2.26
778	2.03	846	2.46
780	2.06	847	2.33

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peratures of the measurements and the ratio of the partial pressures of the two gases, $K = [CO_2]/[CO]$, at each temperature.

Nothing is known as to the specific heats of the two fused salts, but we can make no great error in assuming that the change in heat capacity in our reaction is negligible. If so, the heat of reaction is constant and log K will be a linear function of $1/T$. We have plotted these two quantities against one another and have drawn the best straight line through the individual points. From this line produced we find at the eutectic point, 555° A, $K_{555} = 0.89$. From the slope of the line we find for the reaction involving the fused salts $\Delta H = 3130$ cal., which is not very different from the value $\Delta H = 4300$, obtained from the data of Thomsen and Berthelot for the corresponding reaction involving the solid salts at room temperature.

Since all the measurements were made with a mixture having the same composition as the eutectic mixture, the ratio of the pressures of the two gases over the solid salts at the eutectic temperature will be the same, namely, $K = 0.89$. Hence for the reaction

$$KCNO(s.) + CO(g.) = KCN(s.) + CO_2(g.); \quad \Delta F^{\circ}_{555}{}' = -R'T \ln K = 126.$$

The specific heats of the two solids are not known, but if we apply Kopp's law we see that the heat capacity of the cyanate will be greater than that of the cyanide by about as much as that of carbon dioxide is greater than carbon monoxide. Hence we may write $\Delta\Gamma = 0$. We have seen that $\Delta H = 4300$, and in the equation $\Delta F = \Delta H_0 + IT$, substituting the above value of ΔF, we find $I = -7.52$, and finally

$$KCNO(s.) + CO(g.) = KCN(s.) + CO_2(g.); \quad \Delta F^{\circ}_{298} = 2060. \quad (1)$$

The Free Energy of Solution of Potassium Cyanide and Cyanate.

The determination of the difference in free energy between a very soluble solid salt and its ions at hypothetical molal concentration in aqueous solution has rarely been made. Fortunately at the time this work was being carried on a general study of the free energy of solution was being carried on in this laboratory by Dr. W. H. Rodebush, and in collaboration with him data were obtained from which the free energy of solution of potassium cyanide and cyanate may be calculated. The chief data required are the freezing points determined over the widest possible range of temperature. For the two salts in question the freezing points of their aqueous solutions were obtained down to the cryohydric points which were found to be —29.61° for potassium cyanide and —18.14° for potassium cyanate. The results are given in Tables II and III, the first column showing the number of grams of salt per 1000 g. of water, and the second the freezing point.

The solubilities at 25° were also determined and found to be 716 g. potassium cyanide per 1000 g. of water and 750 g. potassium cyanate per 1000 g. of water. The latter quantity was a little difficult to obtain on account of the rapid decomposition of the solution, but reproducible results were ob-

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tained by violent shaking in the thermostat for a short time, and four determinations differed from the mean by only 0.3%.

TABLE II.—KCN.

460.1	—24.83°
408.1	—21.93
359.3	—18.99
309.2	—16.18
266.5	—14.36
251.0	—13.37
209.0	—10.88
113.1	— 5.64

TABLE III.—KCNO.

320	—17.40°
270	—13.58
264	—13.00
212.5	— 9.94
141.8	— 6.29
98.4	— 4.18

The utilization of these data, together with familiar thermodynamic equations, for the calculation of the free energy of solution of the two salts will be fully discussed in the paper by Dr. Rodebush and need not be discussed in detail here. As a result of these calculations we find for the dilution of the saturated solution to the point where the ions are at hypothetical molal concentration, or, in other words, in passing from solid salt to the ions of hypothetical molal concentration,

$$KCN(s.) = K^+ + CN^-; \quad \Delta F^\circ_{298} = -2130 \qquad (2)$$

$$KCNO(s.) = K^+ + CNO^-; \quad \Delta F^\circ_{298} = -1440 \qquad (3)$$

The Free Energy of Formation of Cyanide Ion and of Aqueous Hydrocyanic Acid.

If we combine Equations 1, 2 and 3 we find

$$CNO^- + CO(g.) = CN^- + CO_2(g.); \quad \Delta F^\circ_{298} = 1370. \qquad (4)$$

Of these four substances the free energy of the first, second and fourth are known from existing data. Thus for cyanate ion we may combine the following six equations:

$$CO(NH_2)_2(M) = NH_4^+ + CNO^- \qquad \Delta F^\circ_{298} = 2766^1$$

$$CO_2 + 2NH_3 = CO(NH_2)_2(M) + H_2O(l) \qquad \Delta F^\circ_{298} = -3334^1$$

$$C_G + O_2 = CO_2 \qquad \Delta F^\circ_{298} = -94360^2$$

$$N_2 + 3H_2 = 2NH_3 \qquad \Delta F^\circ_{298} = -9480^3$$

$$NH_4^+ + \ominus = 2H_2 + \tfrac{1}{2} N_2 \qquad \Delta F^\circ_{298} = 19895^3$$

$$H_2O(l) = H_2 + \tfrac{1}{2} O_2 \qquad \Delta F^\circ_{298} = 56620^4$$

Whence by addition,

$$C_G + \tfrac{1}{2}N_2 + \tfrac{1}{2}O_2 + \ominus = CNO^-; \quad \Delta F^\circ_{298} = -27893. \qquad (5)$$

From the paper by Lewis and Randall on "The Free Energy of Carbon Compounds" we have

$$CO + \tfrac{1}{2}O_2 = CO_2; \quad \Delta F^\circ_{298} = -61800.$$

[1] Lewis and Burrows, THIS JOURNAL, **34**, 1515 (1912).
[2] Lewis and Randall, *Ibid.*, **37**, 458 (1915).
[3] Lewis and Adams, *Ibid.*, **37**, 1983 (1915).
[4] Lewis and Randall, *Ibid.*, **36**, 1969 (1914).

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Combining this equation with (4) and (5) we find the free energy of formation of cyanide ion,

$$C_G + \tfrac{1}{2}N_2 + \ominus = CN^-; \quad \Delta F^\circ_{298} = 35277. \qquad (6)$$

Since we take the free energy of formation of hydrogen ion as zero, this equation also gives the free energy of formation of hydrocyanic acid in a solution molal with respect to each ion, namely,

$$\tfrac{1}{2}H_2 + C_G + \tfrac{1}{2}N_2 = H^+ + CN^-; \quad \Delta F^\circ_{298} = 35277.$$

In order to determine the free energy of undissociated hydrocyanic acid we may use the results of Walker and Cormack[1] who found from conductance measurements that the dissociation constant at 18° is 13.2×10^{-10}. For the heat of dissociation von Steinwehr[2] found 11100 cal. and Thomsen[3] 10930. Taking 11000 as the best value we find by means of the van't Hoff equation $K_{298} = 2.06 \times 10^{-9}$. Hence

$$HCN(aq.) = H^+ + CN^-; \quad \Delta F^\circ_{298} = 11856. \qquad (7)$$

Finally, combining Equations 6 and 7, we have

$$\tfrac{1}{2}H_2 + C_G + \tfrac{1}{2}N_2 = HCN(aq.); \quad \Delta F^\circ_{298} = 23421. \qquad (8)$$

BERKELEY, CAL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

THE SPECIFIC HEATS AT LOW TEMPERATURES OF SODIUM, POTASSIUM, MAGNESIUM AND CALCIUM METALS, AND OF LEAD SULFIDE.

BY E. D. EASTMAN AND W. H. RODEBUSH.

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The empirical law of Dulong and Petit, in its original form, states that the heat capacity per gram atom of all the solid elements, excluding those of very low atomic weight, is the same and equal to 6.4 calories per degree. This is the average value of C_p, the atomic heat at constant pressure. Lewis[4] has shown that if C_v, the atomic heat at constant volume, be considered, not only are the deviations from the average considerably smaller, but that the new value 5.9 calories per degree is identical with that calculated on the basis of the theory of equipartition. According to this principle the change of kinetic energy with the temperature is 3R/2 per gram atom for any substance whose individual atoms are able to move in every direction. The usual assumption that the atoms of a solid element are in harmonic oscillation about more or less fixed positions requires that they possess potential as well as kinetic energy, and that the time averages of the two be equal. This would give as the atomic heat 3R or 5.97 calories

[1] Walker and Cormack, *J. Chem. Soc.*, **77**, 16 (1900).

[2] Von Steinwehr, *Z. physik. Chem.*, **38**, 198 (1901).

[3] Thomsen, "Thermochemistry," **1908**, p. 252.

[4] Lewis, THIS JOURNAL, **29**, 1165 (1907); *Z. anorg. Chem.*, **55**, 200 (1907).

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per degree. The agreement between fact and theory has in the past been regarded as proof of the validity of the equipartition law applied to solids.

Much recent experimental and theoretical research shows however that the principle does not hold under all circumstances. Lewis and Adams[1] have expressed the belief that the atoms do not in general gain as much energy as required by it, but that the law is a limiting one, more closely approached the higher the temperature, the heavier the atoms, and the weaker the constraints operating upon them. Upon this basis it is evident that the energy gained by the atom in a temperature rise of one degree will depend upon the particular values of these three variables, and that the value 3R for the atomic heat will be reached as the limit. Whether these assumptions are correct or not, the deductions are in accord with the actual behavior, over very wide ranges of temperature, of the many substances hitherto studied. The Dulong and Petit generalization is possible because at ordinary temperatures, the region of most rapid rise of specific heat has already been passed for most elements, and the limit nearly reached.

While atomic heats smaller than 3R may be accounted for as above, any instances where C_v is found to exceed 6 must be regarded as exceptional and requiring special explanation. Lewis, in the paper referred to, gives 6.4 as the value for sodium, and 6.5 for potassium. Subsequently, Dewar[2] has reported the value 6.3 as the mean C_p of cesium between the boiling points of hydrogen and nitrogen. Though this is the specific heat at constant pressure, it is probable that $C_p - C_v$, even for an element like cesium, is very small at such low temperatures. Also the work reported by Nernst and Schwers[3] on magnesium showed normal values at the lower temperatures, becoming abnormally high at the upper limit of their investigation. It was suggested to us by Professor G. N. Lewis that the strong electro-positive character of all these metals might be of much significance in connection with their unusually high specific heats, and that a detailed study of the alkali metals would prove of interest. With this object in view, measurements at temperatures between 65° and 300° absolute have been made, by methods described below, of the specific heats of sodium, potassium, magnesium and calcium.

In connection with another problem the specific heats of lead sulfide (galena) have also been determined. As the investigation has been interrupted before it could be extended to other substances, it has seemed well to include, without further discussion, the results obtained for it with the tabulations of the data for the metals.

[1] Lewis and Adams, *Phys. Rev.*, 4, 331 (1914).

[2] Dewar, *Proc. Roy. Soc. London*, (*A*) 89, 158.

[3] Nernst and Schwers, *Sits. Ber Preuss. Akad. Wiss.*, 1, 255 (1914).

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Experimental Methods.

The Temperature Scale.—Preliminary to the specific heat experiments was the establishment of the temperature scale. As the instrument for the measurement of temperatures, the copper-constantan thermocouple was chosen. It lacks the ease of calibration of the platinum resistance thermometer. Its form, its ease of replacement and the absence of disturbing heating effects are the factors which led to its choice in spite of this. As a standard a four-couple element of No. 30 "Ideal" wire, made by the Electrical Alloy Co., of Morristown, New Jersey, and No. 35 copper wire was used. The homogeneity of the constantan wire was tested by the method of White.[1]

Between the freezing point of mercury and the transition point of sodium sulfate decahydrate the couple had been calibrated by the Bureau of Standards. At lower temperatures comparison was made with nitrogen, oxygen and carbon dioxide vapor-pressure thermometers, as described by von Siemens.[2] The gases used were purified by his methods. Before the final filling the thermometers were evacuated several times while being heated in all parts to remove gases retained by the glass surfaces. The mercury used in the manometers was washed in HNO_3 and distilled in a current of air, being carefully boiled out in the thermometers prior to their filling with gas. The manometers were provided with an improved form of trap for eliminating gases in the closed end. The comparison with the oxygen thermometer was made by placing the condensation tube of the latter by the side of the thermocouple junction in liquid air, both being surrounded by a mantle of sheet copper. The liquid air boiling under atmospheric pressure was found to maintain a sufficiently constant temperature. Pressure and e. m. f. readings were made simultaneously. The nitrogen points were obtained with the thermometers imbedded in solid mercury contained in a copper tube immersed in liquid air boiling under reduced pressure. For the carbon dioxide comparison constant-temperature baths of solid CO_2 and various organic liquids were available. Potential measurements were made with the potentiometer described in a previous paper.[3] The height of the mercury columns was read on meter sticks carried between the two arms of the manometers, an accuracy of 1 mm. or better being obtained.

From the pressure readings the temperatures were given by the work of von Siemens as recalculated by Holst[4] on the basis of the latest calibration of the Leiden standard resistance thermometer. Siemens' results in the case of oxygen are in good agreement with those of Kammerlingh-Onnes.[5]

[1] White, This Journal, 36, 2292 (1914).

[2] Von Siemens, *Ann. Physik.*, [4] 42, 871 (1913).

[3] Randall, von Bichowsky and Rodebush, This Journal, 38, 1266 (1916).

[4] Holst, *Verslag. Akad. Wetenschappen*, 24, 603 (1915).

[5] Kammerlingh-Onnes, Leiden, Comm. Phys. Lab., 107 (1908).

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The carbon dioxide vapor-pressure curve obtained by him joins on well with that of Henning[1] in the neighborhood of atmospheric pressure, and with Nernst's[2] at small pressures. The nitrogen values differ by 0.1° to 0.2° from the older and apparently less accurate ones of Fischer and Alt.[3] The freezing point of mercury given by Henning is 234.20° K, on the Leiden scale it is 234.24° K, and Wilhelm[4] at the Bureau of Standards finds 234.22° K; the value adopted for this work is 234.2° K.

Hitherto, no simple equation expressing the behavior of the copper-constantan thermocouple over a considerable temperature range has been proposed. It was found, however, that an equation of the type

$$E = E_0 + aT^n, \qquad (1)$$

in which E and T represent the e. m. f. and absolute temperature respectively, and E_0, a and n are constants, fitted very closely these experiments. No equation valid over the entire range within the limits of experimental error was found; the simple equation was restricted therefore to the upper temperatures. Below the sublimation point of carbon dioxide, where the variation in thermo-electric power is more rapid, a term involving a fourth constant was introduced, the equation becoming

$$E = E_0 + aT^n + bT. \qquad (2)$$

The numerical values of the constants used in Equation 1 are: $E_0 = 26672$, $a = -2.2143$, $n = 1.675$. In Equation 2 $E_0 = 26840$, $a = -0.74097$, $b = -17.45$, $n = 1.837$.

TABLE I.—CALIBRATION OF THERMO-ELEMENT.

Standard.	T.	$E_{obs.}$	$E_{calc.}$ Eq. 2.	ΔT.	$E_{calc.}$ Eq. 1.	ΔT.
N_2 thermometer No. 1:						
p = 135.3	65.32	24093	24100	—0.11	...	..
p = 238.5	68.80	23879	23879	0.00	...	..
N_2 thermometer No. 2:						
p = 557.2	74.85	23487	23480	+0.10	...	..
O_2 thermometer:						
p = 261.7	81.05	23044	23047	+0.01	23036	—1.80
p = 341.2	83.10	22901	22900	—0.03	...	..
p = 458.4	85.52	22721	22723	—0.03	...	..
CO_2 thermometer:						
p = 349.1	185.5	12718	12721	—0.02	12717	+0.01
p = 520.4	190.1	12139	12139	0.00	12133	+0.05
Hg freezing point	234.2	6052	6050	+0.01	6061	—0.06
H_2O freezing point	273.1	0	—75	+0.45	—1	+0.00
$Na_2SO_4.10H_2O$ transition point	305.5	—5509	...	..	—5512	+0.02

[1] Henning, *Ann. Phys.*, **43**, 282 (1914).
[2] Nernst, *Physik. Z.*, **9**, 435 (1908).
[3] Fischer and Alt, *Ann. Phys.*, [4] **9**, 1142 (1902).
[4] Wilhelm, Bureau of Standards, *Scientific Paper* **204** (1916).

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The results of the comparison are given in Table I. The first column shows the comparison standards, the pressures being expressed in millimeters of mercury at 0° C. The second column gives the absolute temperature, and the third observed e. m. fs., in microvolts. Cols. 4 and 6 contain the values calculated for the e. m. fs. by Equations 2 and 1, respectively. The columns headed ΔT give the differences in degrees between observed and calculated values of the temperature.

The figures in Table I are for the four-couple element. In the actual specific heat measurements single couples were always used, being checked against the standard after runs. From the equations above, a table was constructed giving the electromotive force and its temperature coefficient for a single couple at 10° intervals between 60° and 300° absolute. By its use T and dE/dT were conveniently determined with an accuracy approaching 0.1° and 0.5%, respectively.

The Measurement of Specific Heats.—In principle, the method[1] first used by Eucken and since then further developed in Nernst's laboratory was adopted. By this scheme the temperature rise caused by supplying electrically a measured amount of heat to the substance under investigation is determined at the desired temperatures, the material being suspended *in vacuo* and protected as well as possible from radiation exchanges with the surroundings.

The magnesium and calcium, in the form of cylindrical blocks were wrapped with No. 36 (B. and S. gauge) silk insulated constantan wire, which formed a heating coil of 110 ohms' resistance. Thermal contact was secured with paraffin or shellac. The leads, four in number, were of No. 40 copper wire. A thermocouple was bound on by means of the heating wire. The block was then enclosed in a sheath of thin sheet copper, highly polished on the outside.

The sodium and potassium were melted *in vacuo* and forced through a small tube into a thin-walled brass container provided with a tightly fitting cover. The inclusion of an appreciable amount of oxide was avoided in this way, and good thermal contact with the container secured. The thermocouple was soldered to the outside of the can, the latter wrapped with constantan wire and covered with copper, as before. The heat capacity of the can with the same fittings had been accurately determined previously.

The container for the lead sulfide was of copper, the thermocouple and heating coil again being on the outside protected by the shield of polished copper foil. Partitions of thin copper extended from the walls to the interior of the container. Small cubes of galena were inserted, the cover carefully soldered on and the can filled with hydrogen through a small copper tube which was then closed. The hydrogen and the copper partitions gave quick and thorough distribution of heat.

[1] Nernst and Schwers, *Loc. cit.*

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Thus prepared, the materials were suspended in the lower end of a tube of pyrex glass, 5 cm. diameter and 60 cm. long. (The calorimeters were approximately 9 × 4 cm.) The tube was closed at the mouth by another tube of smaller diameter (leading to the vacuum pump) kitted in with de-Khotinsky cement, the lead wires passing through this seal. The procedure then was to admit hydrogen to the tube to act as a conductor between the calorimeter and the cooling bath surrounding the tube. When the desired temperature had been reached, the hydrogen was pumped out. When the tube was sufficiently evacuated, as indicated by the character of the discharge produced within it when connected on the outside to the terminal of a spark coil, the measurements were begun, proceeding from lower to the higher temperatures.

The quantity of electrical energy supplied in a determination was known from the current in the coil and the voltage at its terminals, measured on carefully calibrated Weston instruments, the time of heating being measured with a stop-watch. A battery of lead storage cells discharging slowly through a high resistance, from the terminals of which the heating current was taken, gave a sufficiently constant voltage. The change in resistance in the copper leads during heating caused a small variation in the current during runs at low temperatures; this variation, which was seldom as much as 1%, was corrected for by averaging readings taken at suitable intervals. The resistance of the constantan heating coil did not vary appreciably during runs, which is an important advantage.

The prevention, as far as possible, of heat exchange between the calorimeter and its surroundings obviously is very necessary, so that a very high vacuum is required. This was secured by means of a remarkably efficient and satisfactory mercury vapor pump designed in this laboratory by Dr. G. E. Gibson. Radiating surfaces of the calorimeter were of highly polished copper, which is an even better reflector, at low temperatures, than silver. The walls of the containing tube were silvered inside. A series of baffle plates of copper were placed above the calorimeter, which were cup-shaped in design, and when in place expanded against the walls of the tube, giving good thermal contact. From the lower baffle, which was a plate supported on a constriction in the tube, the calorimeter was hung by a silk thread. The temperature of the surroundings was maintained approximately equal to that of the calorimeter. Below 100° K. the effect of radiation is small enough to allow considerable latitude in this, and the liquid air bath surrounding the tube sufficed. Between 100° K. and the boiling point of carbon dioxide, and at room temperature, a copper tube of large heat capacity was employed. This tube, which fitted closely over the glass-containing tube, was provided with a heating coil and thermocouple, permitting the regulation of its temperature. A little liquid air in the bottom of the long Dewar tube in which it was enclosed kept it

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from warming indefinitely. Usually the mantle was maintained at a temperature such that the calorimeter remained constant in its temperature after heating. When necessary, *i. e.*, when radiation effects were very large, the mantle and calorimeter could be heated simultaneously. In the lower range it was found that the calorimeter always had a warming rate until it reached a temperature considerably higher than that of the surrounding bath. This temperature difference was found to be reduced by the use of a long Dewar tube, and by looping the lead wires to the bottom of the glass tube and pressing them against the walls of the tube by means of the baffles.

The Experimental Results.

The results of the measurements thus far made are shown in Tables II–VI. As a typical example of the way in which C_p values there given were obtained, one of the magnesium runs will be described in detail. At 1.49 P.M. the magnesium was heated for 124.4 sec., the total energy supplied being calculated to be 44.60 calories. (The current in coil was 0.1196 ampere, the voltage at terminals 12.53. The value $j = 0.2391$ cal.$_{15°}$ was used as the electrical equivalent of heat.) The readings of the potentiometer are given at minute intervals before and after heating.

Time.	E. M. F.	Time.	E. M. F.
1.47	5742.7	2.00	5690.7
1.48	5742.7	2.01	5690.8
1.49	5742.7	2.02	5690.9
1.58	5690.2	2.03	5690.9
1.59	5690.4	2.04	5690.9
2.00	5690.7	2.05	5690.9

The initial and final readings are seen to be 5742.7 and 5690.9, respectively, the average being 5717 and the change 51.8 microvolts. Interpolation in the table previously mentioned shows 83.5° K. as the temperature, and 18.16 microvolts as the value of dE/dT, corresponding to an e. m. f. of 5717 microvolts. $44.60 \times 18.16/51.8 = 15.64$ cal. is thus the heat capacity of the block of magnesium and its copper sheath. The latter, including 0.6 g. of constantan which was figured as copper, weighed 10.7 g. Its heat capacity at 83.5° K. was taken from the work of Nernst and Lindemann[1] to be 0.52 cal., leaving 15.12 cal. as the heat capacity of the 110.3 g. of magnesium in the block. This gives $C_p = 3.33$ cal./deg. as the atomic heat capacity at constant pressure. In the example given the temperature was constant both at the beginning and end of the run. This was very often the case. When there was a cooling or warming rate it was usually very regular and could be corrected for easily without

[1] Nernst and Lindemann, *Z. Electrochem.*, 17, 818 (1911).

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plotting. Corrections were never over three per cent. of the total rise in temperature.

$C_p - C_v$ for sodium, potassium and magnesium has been calculated at 293° K. by Lewis[1] from the compressibilities and coefficients of expansion. Values at other temperatures were obtained from the approximate proportionality[2] of $C_p - C_v$ to $T^{3/2}$. To obtain C_v in the case of calcium, a second approximate relation connecting C_p, C_v, T and T_s, was used, T_s representing the melting point.

The error of the measurements is thought not to exceed 1%. The sodium and potassium used were Kahlbaum's. Qualitative tests of the magnesium showed only negligible amounts of Al, Fe, SiO_2. Analysis of the calcium showed 97.75% Ca, 0.85% Cl, 1.08% of Fe and Al as oxides, and a trace of Mg. Very perfect small cubes of galena were selected for the measurements, the presumption being that errors due to impurity in the crystals would not exceed the errors from other sources. The weights of the substances used in the specific heat determinations were 2.396 mols of sodium, 1.046 mols of potassium, 4.535 mols of magnesium, 3.550 mols of calcium, and 1.316 mols of lead sulfide. The heat capacities of the containers and fittings varied between the following indicated percentages at the lowest and highest temperatures in the different cases: Sodium, 10–18%; potassium, 22–34%; magnesium, 3–5%; calcium, 5–7%; lead sulfide 14–20%.

ATOMIC HEAT CAPACITIES.

Table II.—Sodium.

T.	C_p.	C_v.	T.	C_p.	C_v.
64.6	4.52	4.47	159.0	5.99	5.79
67.9	4.66	4.60	181.7	6.15	5.91
71.1	4.77	4.71	183.8	6.17	5.92
74.2	4.81	4.75	234.7	6.43	6.07
84.6	5.08	5.00	292.1	6.78	6.28
94.8	5.30	5.21	293.5	6.79	6.29
156.8	6.02	5.82			

Table III.—Potassium.

T.	C_p.	C_v.	T.	C_p.	C_v.
68.6	5.76	5.69	116.7	6.20	6.05
72.3	5.74	5.67	119.3	6.23	6.07
76.0	5.78	5.70	152.2	6.40	6.18
79.8	5.86	5.77	199.5	6.68	6.34
87.0	5.96	5.86	203.5	6.72	6.37
94.1	6.08	5.97	285.1	7.05	6.47
101.8	6.06	5.95	286.7	7.10	6.52

[1] Lewis, This Journal, 29, 1165 (1907).

[2] Lindemann and Magnus, *Z. Electrochem.*, 16, 269 (1910).

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TABLE IV.—MAGNESIUM.

T.	C_p.	C_v.	T.	C_p.	C_v.
74.9	2.90	2.87	155.2	5.08	5.00
78.3	3.03	3.00	172.4	5.31	5.22
83.5	3.33	3.30	192.6	5.55	5.44
92.1	3.61	3.57	220.0	5.82	5.69
101.5	3.99	3.93	237.3	5.83	5.69
114.5	4.47	4.42	253.5	5.98	5.82
115.8	4.44	4.39	255.2	5.86	5.70
132.7	4.77	4.71	288.5	6.11	5.91

TABLE V.—CALCIUM.

T.	C_p.	C_v.	T.	C_p.	C_v.
67.6	3.93	3.91	143.3	5.68	5.59
70.4	4.02	4.00	145.2	5.73	5.63
73.3	4.16	4.13	163.2	5.97	5.85
76.2	4.28	4.25	198.5	6.36	6.20
80.6	4.42	4.39	200.0	6.38	6.22
92.7	4.81	4.77	230.3	6.46	6.27
94.9	4.92	4.87	287.2	6.74	6.48
103.4	5.07	5.02	293.5	6.75	6.48
141.4	5.70	5.61			

TABLE VI—LEAD SULFIDE (GALENA).

T.	C_p.	T.	C_p.	T.	C_p.	T.	C_p.
63.8	7.71	90.1	9.12	131.3	10.33	182.3	11.17
66.6	7.96	96.9	9.45	133.6	10.34	196.6	11.40
70.0	8.09	100.0	9.59	142.3	10.64	196.7	11.50
73.1	8.34	105.3	9.68	149.1	10.61	197.6	11.45
75.9	8.40	109.2	9.70	155.0	10.90	198.7	11.48
78.8	8.63	111.8	9.84	161.7	10.84	235.0	11.80
81.7	8.80	114.3	9.88	168.4	10.95	237.0	11.86
84.6	8.88	121.9	9.98	175.3	11.24	280.7	12.01
87.4	9.07	124.2	10.10	180.0	11.13	282.7	12.16

Discussion of Results.

The results of our experiments are represented by the individual points in the accompanying diagrams, where C_v is plotted against the common logarithm of the absolute temperature. For a detailed account of the advantages of this method of plotting, and for the full significance of the continuous curves, reference is made to a paper by Lewis and Gibson.[1] Here it will suffice to state that the form of the curve, which is fully shown in Fig. 1, is a general one and that only horizontal displacement is required to make it fit exactly the data for any one of a large class of elements which have been investigated over wide ranges of temperature. The criteria which may generally be used to predict whether or not any element belongs in this group would include the alkali metals in it.

[1] Lewis and Gibson, THIS JOURNAL, 39, 2554 (1917).

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Our values of C_v for magnesium, as shown in Fig. 1, follow the regular curve in the lower range of our experiments, but rise above it at the upper temperatures.[1] This behavior is typical also of sodium and calcium, as

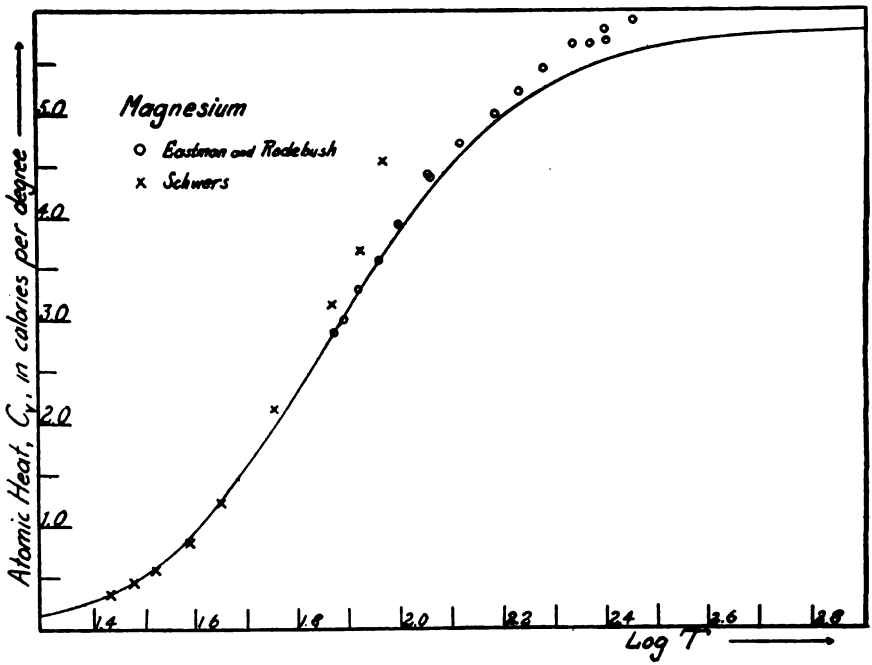

Fig. 1.

will be seen from Fig. 2. The points for potassium seem to lie above the regular curve even at the lowest temperatures attained by us, it being impossible to locate the regular curve corresponding to them by the usual displacement method. The curve may, however, be approximately placed from the measurements of Dewar and the calculations of Lewis and Gibson previously referred to. For purposes of comparison this has been done.

For each metal C_v rises well above the normal experimental and theoretical value of 6. These high specific heats obviously cannot be accounted for solely on the basis of the modified equipartition law mentioned in the introduction to this paper. If the postulate is retained that the oscillations of the atoms are harmonic,[2] we are led at once to the conclusion that not only the atoms but some at least of their constituent electrons are

[1] It will be noted that our values do not confirm those reported by Nernst and Schwers (*Loc. cit.*) at liquid air temperatures, but that their points also fall on the regular curve at lower temperatures.

[2] Langmuir, THIS JOURNAL, 38, 2236 (1916), discusses the possibility that this assumption is not correct in all cases, and points out that if the restoring force does not increase as rapidly as the displacement of the atoms from their equilibrium centers, the

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acquiring thermal energy. If it is granted that the atomic weight and the acting constraints are factors determining the energy absorbed, the electrons should be expected to gain considerable amounts only at comparatively high temperatures. For not only are the electrons by far the lightest of all the atoms, but in most substances they are under large constraints, as indicated by the optical properties. There is much evidence, however, that in metals the electrons are more loosely bound, and that their freedom increases with the electro-positive character of the metal. The temperatures at which their absorption of energy becomes appreciable should be lower therefore, for the alkali metals than for any others, which is in accordance with the behavior we have found.

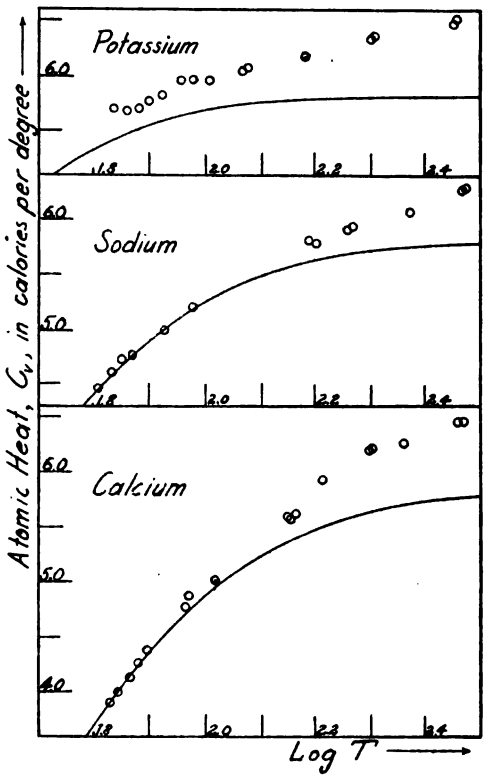

Fig. 2.

Our experiments show further that the deviation from the regular curve at any one temperature is greater for potassium than for sodium and greater for calcium than for magnesium, which presumably is also the order of the freedom of the electrons. We regard these deviations from the normal curve as representing the actual specific heat of the electrons, and believe that the effect will also be shown by the less positive metals, though at higher temperatures. A new and interesting field is thus opened in the comparison of the evidence regarding electronic freedom offered by specific heats, as more extensive data are obtained, with that deduced

time average of potential energy may become greater than that of the kinetic energy. As the latter must still be $3R/2$, a value of atomic heat greater than $3R$ would result. At small amplitudes the vibrations of the atoms most probably are harmonic, but with increasing amplitude the conditions mentioned might arise. With metals as far from their melting points as those in this investigation, it seems unlikely that the amplitudes of the atoms should be so large as to destroy the harmonic character of their vibrations. Even if this were the case, there is the possibility that the restoring force would increase more rapidly than the displacement, resulting again in specific heats smaller than 6.

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from the study of other phenomena, for example, the volta and photoelectric effects.

The writers wish again to acknowledge their indebtedness to Professor G. N. Lewis.

BERKELEY, CAL.

[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTE OF WASHINGTON.]

THE COLOR OF INORGANIC COMPOUNDS.

BY F. RUSSELL V. BICHOWSKY.

Received January 10, 1918.

In order for a substance to show selective absorption of light in any part of the visible or invisible spectrum it is necessary, according to present electromagnetic theories, that the substance contain some sort of electromagnetic mechanism capable of vibration with a free period corresponding to that of the light absorbed. The mechanism usually assumed is the constrained electron. In other words, substances capable of selective absorption in the visible or ultraviolet are supposed to contain electrons which are held by elastic or pseudo-elastic electrical constraints to some definite point of equilibrium and which are capable of vibration, given a suitable electromagnetic stimulus, with a certain definite free period determined by the magnitude of the constraining forces.

In some cases it is uncertain just what electrons are involved in the absorption. In the case of absorption in the visible and in that part of the ultraviolet extending to say 2100° A, the overwhelming evidence of organic chemistry showing that color is a function of structure proves that the electrons involved in selective absorption in this region, at least, are the same electrons that take part in chemical union, *i. e.*, are the so-called valence electrons.

Now unfortunately very little is known either about the nature or the magnitude of the forces acting on a valence electron, certainly not enough to justify a quantitative theory of light absorption. However, enough is known about the comparative stability of certain electron arrangements to be able to predict the comparative magnitude of the mean restoring forces acting on valence electrons and thus predict certain qualitative regularities of the absorption spectra of various inorganic compounds.[1]

The magnitude of the mean restoring force acting on a valence electron measures not only the period of mean free vibration of the electron but it

[1] Compared with the vast amount of attention that has been given to the color of organic compounds very little has been given to the more fundamental problem of the color of inorganic compounds. This is probably because it is impossible to make much headway in this field without a rather definite theory of atom structure. An adequate summary of the earlier work attempting to connect color with valence or atomic weight will be found in Kayser, *Handbuch d. Spectroscopie*, III, 141 (1905).

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is also the measure of the degree of stability of that particular electron arrangement, for the degree of stability of an electron arrangement is of course simply the magnitude of the force resisting small displacements from that arrangement, *i. e.*, it is the magnitude of the force which it is necessary to apply in order to start any possible change involving the destruction of the electron arrangement in question. Electron stability thus measures what the chemist means by the reactivity of a compound and is connected with the possibility of the element existing in different valence states, because with strong forces tending to restore any particular valence arrangement it is obvious that other arrangements are less likely to exist. It has, however, no direct connection with the thermodynamic stability of a compound or of a valence state, for thermodynamic stability is measured by the total work, not the initial force, necessary to separate the various parts of the molecule into some other arrangement.

Now it is known by various arguments admirably summed up by Parson[1] and by Lewis[2] that for all atoms there is one particular arrangement of electrons which has maximum electron stability. This arrangement consists, except in the case of H and He, of eight or zero electrons arranged around, or in, the positive nucleus. All other arrangements such as 2, 4, 6, or 10 electrons are very much less stable; of still less stability is the grouping of an odd number of electrons around or in the central nucleus.

Now adopting Lewis' convenient nomenclature where the heavy-typed symbols for the element represent the positive nucleus of the atom in question (supposed to have the number of charges corresponding to the ordinal number of its group in the periodic table, 1 for sodium, 2 for beryllium, etc.) and the dots represent valence electrons (no assumptions being implied as to their spacial distribution, probably except for carbon, helium and hydrogen in the corners of a cube), the chlorine atom becomes $:\dot{\underset{\cdot\cdot}{\mathrm{Cl}}}:$ and the sodium atom $\dot{\mathrm{Na}}$ and sodium chloride becomes $\mathrm{Na}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}}:$, the electrons thus forming a group of eight. NaCl therefore is a substance in which the electrons show maximum electronic stability and which would be expected to show selective absorption only for the higher frequencies. As a matter of fact the absorption bands for NaCl lie well in the ultraviolet. This argument is in no sense limited to NaCl but is perfectly general for substances of its class and it is to be expected that any compound of two or more elements which had all its electrons in groups of eight would show selective absorption at shorter wave lengths than compounds of these same elements having their electrons in groups of any other number. This expectation in the form in which we have put it can only be tested directly

[1] Parson, "A Magneton Theory of the Structure of the Atom," Smithsonian Pub. 2371, Washington (1915).

[2] Lewis, THIS JOURNAL, 38, 762 (1916).

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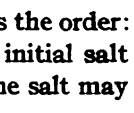
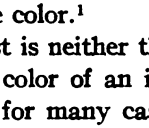
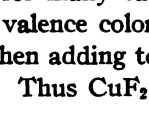
by comparing the color of the same salt, say the chloride, of the same element in different valence states. Thus we should expect



which has all its electrons in groups of eight to have its absorption further in the ultraviolet than



which has a group of six, and we should expect both of these substances to have their absorption further towards the ultraviolet (shorter wave lengths) than



which contains an odd number of electrons and which would hence be expected to show absorption at comparatively long wave lengths. As a matter of fact $TiCl_4$ is colorless (absorption in the ultraviolet), $TiCl_2$ yellow (absorption in the violet), and $TiCl_3$ is blue (absorption in the red and yellow). Because of the paucity of complete series of differently valenced salts of the same elements it is difficult to carry out this test in detail, nevertheless in no well-established case does it fail. That is, the order of colors of salts of the same element in differently valenced states, as the number of electrons in the groups varies from 8 to 6, 4, 2, to 1, 3, 5, 7, always follows the order: colorless, yellow, green, blue, violet, black. The color of the initial salt in the series is, however, not necessarily zero, and more than one salt may have the same color.[1]

But this test is neither the only nor the best test that can be given our theory. The color of an inorganic compound, experience has shown, can be explained, for many cases at least, by giving to each atom present a characteristic valence color, *e. g.*, blue for Cu^{++}, zero for Cu^{+}, zero for F^{-}, etc., and then adding together these valence colors to give the color of the molecule. Thus CuF_2 according to this rule is blue, CuF colorless,

[1] We have disregarded the known complexity of the absorption spectra of certain valence states and have treated all absorption spectra as if they consisted of a single band placed so as to explain the visible color. This is a somewhat broad assumption, as it is by no means evident that all the widely scattered bands lying in various parts of the visible spectra are due to any one group of causes as this assumption implies. Nevertheless, such is the lack of data, unless we made this assumption, we would have been unable to treat the greater part of the color phenomena of inorganic chemistry. Moreover, the fact that marked regularities exist in the color of inorganic compound may be taken as a justification of this assumption. Our procedure is equivalent to renouncing all attempts to explain the shape of the intensity wave-length absorption curve and restricting our attention to the comparative position of the center of gravity of that curve; in other words, it is equivalent to restricting our discussion of the forces of restitution acting on an electron to the average or mean force. To explain completely the known facts of absorption spectra a much more detailed theory of atomic structure is required.

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etc. All of which means, when translated into terms of the valence theory, that the forces acting on any particular valence electron in the class of compound where this rule holds are dependent only on one particular atom nucleus and are not affected by the others. Even in the cases of compounds where the color is not the sum of its valence colors we "explain" the deviation from additivity by saying that in these cases the electrons are no longer acted on by only one nucleus but are acted on by both.

In most cases the chemist's instinct will allow him, without reference to any particular set of rules, to pick out the valence color of any particular atoms. Thus anyone would say that the valence color of Ni^{++} is green, Mo^{+++++} blue, etc., and so on for most of the valence colors given in the following table. However it is perfectly possible to reduce this feeling to certain definite rules.

(A) Since the valence color may be defined as that part of the color of a compound which is due to one nucleus alone, the color of a free ion will obviously be the valence color.

(B) In the case where the ion color is unknown, *i. e.*, in cases where the substance does not ionize, or is not stable in solution, or has its color masked by other substances present, we have to depend on more general rules. As we have said, the color of a compound depends, first, on the valence color of its atoms, and, second, on the amount of interference the forces due to one nucleus have on the stability of arrangement of the electrons belonging to another atom. Thus to find the amount of deviation in the color of compounds from the law of the additivity of valence colors of its elements, it suffices to find some means of measuring this interference. Now obviously the amount of this interatom interference with the natural period of vibration of any electron, will depend on the magnitude of the stabilizing forces normally acting on that electron. If the electron arrangement around the nucleus is very stable, as in sodium compounds, the interference due to the weaker forces from other atoms in the molecule will be very small and hence the color of these compounds will be simply the sum of the valence colors of their constituent atoms. In other words, compounds of two or more electronically stable atoms are likely to be colorless (have their absorption in the ultraviolet), compounds of one or more electronically stable atoms with one electronically less stable are likely to have a color which is the sum of the valence colors of its constituent atoms, while compounds of two or more electronically unstable atoms will in general have a color which is not the sum of the valence colors of the constituent atoms but is, because the effect of one atom on the electron stability of the other atom (on account of the slope of the potential gradient) is to decrease the restraining forces acting on the electrons, a color which corresponds to absorption in the longer wave lengths.

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But now power to exist in many valenced forms is one of the tests of low electron stability. Therefore we should expect (*a*) that compounds of elements of high electron stability, that is, compounds of invariant-valence elements would be colorless; (*b*) that compounds between invariant-valence elements and elements that exist in more than one valence compound would have a color that is the sum of the valence color of their constituent atoms; (*c*) that compounds among multivariant-valence atoms would have a color which is not the sum of the valence colors of their constituent atoms.

Thus we have a means of determining the valence colors of all the elements in almost all valence states. In cases where the compound of an element of invariant valence with an element in a particular valence state is not known, the atom color we have put down in our table is but little more than a guess. It is usually based on the color of some complex salt, in which, because of the extreme polar nature of the environment in such compounds, the interference in normal electron stability is probably small. All of these cases are discussed in detail in what follows.

The atom colors as determined according to the above principles are tabulated in Table I. In this table the rare earth compounds are neglected as we do not know their normal valences. The first column gives the symbols of the elements. The elements of invariant valence, H, He, Ne, Ar, Kr, Xe, Nt, Li, Na, K, Rb, Cs, Be, Mg, Ca, Lu, Sr, Ba, Ra, B, Al, Sc, Si, Zr, F, are grouped together under the symbol Σ. The second column gives the normal valence of the element, that is, the valence which corresponds to the group in the periodic system to which the element belongs. It equals the number of positive charges on the nucleus.

It will be noted that manganese is placed in the eighth group with iron, cobalt and nickel and not in the seventh group with chlorine. If this were not done manganese would form a most striking exception to our theory. But except for the tempting gap after chlorine in the seventh group there is not the slightest reason for placing manganese with chlorine which it resembles perhaps less than any other known element. Then, too, its resemblance to the members of the iron group is quite marked and the only reason that can be urged against putting it in that group is that it would disturb the pretty though apparently quite meaningless rule of three that obtains in that group. This rule it would replace by a rule of four and indicate that the (B) section of the seventh group was fictitious and that one element was missing from the Ru and Os group. It will, of course, be seen that the proposed shift of manganese, *eka*- and *diva*-manganese into the eighth group and the accompanying abolition of the (B) section of the seventh group, makes no change in either the number or the order of the elements as known from Moseley's rule.

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TABLE I.—VALENCE COLORS OF THE ELEMENTS IN THEIR DIFFERENT VALENCE STATES.

	N.	*N*+2.	*N*+1.	*N.*	*N*−1.	*N*−2.	*N*−3.	*N*−4.	*N*−5.	*N*−6.
Σ	–	..	...	O*	..	..	..	..	...	..
Cu	1	..	blue*	O*	..	..	..	..	...	..
Ag	1	..	brown*	O*	..	..	..	..	...	..
Au	1	yellow*	red	O*	..	..	..	..	...	..
Cd	2	..	...	O*	..	..	..	..	...	..
Hg	2	..	...	O*	..	O*	..	..	...	..
Ga	3	..	...	O*	..	O	..	..	...	..
In	3	..	...	O*	..	O*?	..	..	...	..
Tl	3	..	...	O*	..	O*	..	..	...	..
C	4	..	...	O*	various	O*	..	..	...	..
Ti	4	..	...	O*	violet	O*	..	..	...	..
Ge	4	..	...	O*	..	..*	..	..	...	..
Sn	4	..	...	O*	..	O*	..	..	...	..
Pb	4	..	...	O*	..*	O*	..	..	...	..
N	5	..	...	O*	..*	O*	..*	..*	...	..
P	5	..	...	O*	..	O*	..	..	...	..
V	5	yellow	...	O*	blue*	green?*	violet*	..	...	..
As	5	..	...	O*	..	O*	red?	..	...	..
Nb	5	..	...	O*	..*	..	..	..	...	..
Sb	5	..	...	O*	brown?	O*	..	..	...	..
Ta	5	..	...	O*	..*	..	..	..	...	..
Bi	5	..	...	..	..	O*	dark	..	...	..
O	6	..	...	O*	..	O*	..	..	...	..
S	6	..	...	O*	..	O*	blue*	..	...	..
Cr	6	..	blue?*	yellow*	..	..*	violet*	yellow*	...	..
Se	6	..	...	O*	..	O*	..	..	...	..
Mo	6	..	...	O*	blue*	yellow*	violet*	yellow*	...	..
Te	6	..	...	O*	..	O*	..	..	...	..
W	6	..	...	O*	dark?*	yellow*	..*	yellow	...	..
U	6	..	...	O	brown?*	green*	purple*	yellow*	...	..
Cl	7	..	...	O	..	O	yellow*	O	...	O
Br	7	..	...	O	..	O	..	..	...	O
I	7	..	...	O	..	O	..	..	...	O
Mn	8	..	...	..	purple	green*	..	yellow*	red?*	pink*
Fe	8	..	...	..	..	?	..	..	purple?*	yellow?*
Co	8	..	...	..	..	..	..	..	various?*	pink*
Ni	8	..	...	..	..	..	..	..	dark?	green*
Ru	8	..	...	O	..	..	..	yellow*	blue	green?
Rh	8	..	...	..	..	orange	..	..	...	green?
Pd	8	..	...	..	..	..	..	yellow	...	yellow
Os	8	..	...	O	..	..	..	yellow	blue	green
Ir	8	..	...	..	..	green?	..	yellow	blue	orange
Pt	8	..	...	..	..	..	..	yellow	...	orange

The third column of the table gives the valence color of the elements that form compounds in a valence state of two higher than normal; the fourth column, the valence color of elements in valence state one higher than normal; the fifth column, the valence color in the normal valence state;

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the sixth column, in one less than normal, *e. g.*, for vanadium in the tetravalent state; the seventh column $N - 2$, etc.

O in the table indicates that the substance is colorless. The subscripts refer to the color of the oxides and sulfides; (*o*) indicates that the oxide and sulfide are colorless, (*) that one or both are colored.

From this table it will be seen that the agreement between fact and theory is most striking.

I. From the theory one would expect the valence color of the N-valence elements to be more nearly zero than the valence color of any of the other valence forms of the same element. This, because substances in the N-valence state have all their electrons in groups of eight. As a matter of fact in all cases except chromium the valence color of the valence form N is actually zero. Chromium with the valence six as in the chromates has a valence color yellow and an absorption band just in the visible. It is no real exception to the rule.

II. From the theory one would expect the even electron chromopheric compounds, that is, compounds of elements with variable valence, as the oxides, sulfides and iodides, with invariant valence elements to be colorless. The only exceptions to this rule are the yellow sulfide and brown oxide of cadmium.[1] Silver is usually considered of invariant valence but a higher oxide as well as the so-called peroxynitrate[2] are known and thus the black oxide and sulfide as well as yellow iodide do not form a real exception.

III. From the theory we would expect the valence colors listed in the columns labeled $N + 1$, $N - 1$, $N - 3$, $N - 5$, to be more towards the blue than the color for the same elements given in columns N, $N + 2$, $N - 2$, $N - 4$, $N - 6$. This rule is strikingly borne out. For the $N + 1$ column the blue color of cupric compounds needs no comment. Argentic compounds are listed as brown on the somewhat dubious evidence of the peroxynitrate referred to. Our information about Au^{++} compounds is based on the existence of the chloride, bromide and sulfate, but these compounds are reported as dark red, black and brown, respectively. Probably none of them is pure, but surely the valence color of Au^{++} compounds must be more towards the blue than that of the colorless Au^{+} or yellow Au^{+++} atoms. The blue color of the seven-valence chromium atom is based on the color of the so-called perchromic acid. Whatever the true formula of this substance turns out to be, the molecule must be odd and the valence of chromium either seven or nine. In the $N + 2$ compounds the so-called true peroxides like BaO_2 have been neglected. Their formula can be interpreted either on the basis of the change of valence of the metal atom or that of the oxygen. The latter is preferred. Their in-

[1] ZnO is yellow at higher temperatures.

[2] Cf. Brown, *J. Phys. Chem.*, **20**, 686 (1916).

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clusion or exclusion could make no difference in this table except as to the membership of the group Σ. The only compounds included in $N + 2$ are the yellow auric and pervanadic ions. The fact that an atom with no valences can still form compounds should not seem strange after consideration of such compounds as H_2F_2.

Among the compounds in the $N-1$ column the purple or blue Mn^{+++++}, Mo^{+++++}, V^{++++}, T^{+++} compounds call for no special comment. All the compounds in this column are colored except the so-called Hg^{+}, Ga^{++}, In^{++} and Ce^{+++} compounds (the last only if one insists on placing cerium in the fourth group of the periodic table). The Hg^{+}, Ga^{++} and In^{++} compounds reported, *e. g.*, the chlorides, are all probably diatomic complexes like Hg_2Cl_2 which is, on chemical evidence, a mercury-mercuric complex of the formula $:\ddot{\underset{\ddot{}}{Cl}}:\overset{Hg}{\underset{Hg}{}}:\ddot{\underset{\ddot{}}{Cl}}:$. The brown color for Sb^{++++} is based on the brown solution that obtains when $SbCl_3$ and $SbCl_5$ are mixed, and on the double Rb and NH_4 salts which $SbCl_4$ forms.[1] The dark color for W^{+++++} and the brown color for U^{+++++} are based on the colors for impure WCl_5 and UCl_5. WCl_5 has been reported to have almost every color in the spectrum except yellow.[2]

In the case of the $N - 2$ column it will be observed that whenever the $N - 1$ compounds are not known the $N - 2$ atom color is O. This is what might be expected from the theory. The fact that there are no exceptions to this rule is a rather surprising indication of the marked difference of electronic stability between the odd and even molecular forms. Another indication of the same principle is that the only elements in this column whose atomic color is not zero, except the meagerly studied rhodium are also well known in $N - 1$, $N - 3$ or $N - 5$ valences. This rule also holds of course for the $N - 4$ column. It may perhaps be stated as an invariant rule that only compounds of those elements which can exist in odd electronic compounds will be colored. The other columns of this table will not be so carefully discussed. The color As^{++} is based on the dubious evidence of the color of As_2I_2, while that of Bi^{++} depends on that of $BiCl_2$ which as Herz[3] says, "is probably impure." The evidence for the blue color of S^{+++} compounds will be discussed fully in a paper shortly to be published. The yellow color for Cl^{++++} is based exclusively on the color ClO_2. Since Cl^{+++++} and Cl^{+++} are colorless, this color is no exception. The $N - 4$ group has higher electronic stability than either the $N - 2$ or $N - 6$ group. It is therefore not surprising that Mn^{++++} should be yellow while Mn^{+++++} is green and Mn^{++} pink. The vast number of the colors shown by the cobalt complexes makes it somewhat

[1] Schenck, *Abegg's Handbuch*, [3] III, 609 (1907).
[2] Gmelin-Kraut, *Handbuch*, [1] III, 754 (1912).
[3] Herz, *Abegg's Handbuch*, [3] III, 648 (1907).

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difficult to decide on the real atom color of Co^{+++}, but it is probably purple. The ion Co^{++} is of course pink. Why so many Co^{++} compounds should be blue is not known. It is interesting to note that the only colorless compound of chromium is $:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:Cr:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:$. The ion is yellow. The valence color of ferric iron is based on the color of its complex salts, the so-called ferric ion, which is yellow, is the complex FeFe.

Summary.

(1) Every valence state of an element can be associated by means of purely experimental evidence with a definite "atom color."

(2) There is a marked relation between atom color thus determined and valence and valence variability.

(3) The atom color of every element in its normal valence state, that is in the valence state which corresponds to its place in the periodic system, is zero (all non-variant-valence atoms have their normal valence).

(4) The atom color of an element, in valence states where the valence is decreased or increased by an odd number from the normal valence, lies further in the blue than the atom color of the same element in any other valence state.

(5) The atom color of an element in a state whose valence is removed by an even number from normal will be zero if compounds of the element do not exist in which the valence of the element is removed by an odd number from normal; otherwise the atom color will lie further in the yellow than the atom color of the same element in a state of valence removed by an odd number from normal.

(6) Manganese *eka* and *diva* manganese belong in the eighth group with iron and the rare earths, and not in the seventh group with chlorine.

(7) Mercurous, gallous, and indous salts are double complexes. So is the ferric ion.

(8) Compounds between non-variant-valence elements will be colorless.

(9) Compounds between a non-variant-valence element and a variant-valence element will have the same color as the "atom" of variant-valence element.

(10) Compounds between other elements will have colors more to the blue than the sum of their atom colors.

(11) All these regularities can be deduced from a variation of Lewis' theory of atom structure.

(12) The almost perfect accord between the deduction and the facts indicates very strongly that Lewis' fundamental hypotheses are correct.

WASHINGTON, D. C.

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[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY LABORATORY OF THE STATE UNIVERSITY OF IOWA.]

THE ELECTROMOTIVE FORCE AND FREE ENERGY OF DILUTION OF LITHIUM CHLORIDE IN AQUEOUS AND ALCOHOLIC SOLUTIONS.

BY J. N. PEARCE AND F. S. MORTIMER.

Received January 17, 1918.

The study of the electromotive forces in aqueous solutions of electrolytes has always presented an attractive field for research. One has but to scan the literature[1] of the last twenty-five years to be convinced of the enormous amount of work which has been done in this field alone. It is only in more recent years that attempts have been made to extend electrometric measurements with the view of correlating the results of the measurements of electromotive force of concentration cells with other colligative properties of solutions.

Dolezalek[2] has determined the electromotive forces at 30° of hydrogen-chlorine cells, using hydrochloric acid for the electrolyte and in concentrations ranging from 4.98 N to 12.25 N. His results are sufficiently accurate to permit the calculation of the free energy of transference of hydrochloric acid for the various concentrations used.

Using concentration cells of the type

$$\mathrm{Ag} \mid \mathrm{AgCl}, \mathrm{HCl}c_1 \mid \mathrm{HCl}c_2, \mathrm{AgCl} \mid \mathrm{Ag}$$

Jahn[3] determined with great accuracy the electromotive forces for concentrations ranging from 0.033 N to 0.00167 N. Similar cells were made using correspondingly dilute solutions of the chlorides of sodium and potassium. From the results obtained he concluded: (1) that the mobility of the ions is dependent to a high degree upon their concentration, increasing with increasing concentration, (2) that the conductivity of an electrolyte is not a true measure of its dissociation.

Tolman and Ferguson[4] determined the electromotive forces for concentration cells of the type $\mathrm{Hg} \mid \mathrm{HgCl}, \mathrm{HCl} \mid \mathrm{HCl}, \mathrm{H_2} \mid \mathrm{Pt}$ at 18° and combined so as to eliminate transference. From these they calculated the free energy of dilution of hydrochloric acid, and the ratios of the fugacities of the ions and of the molecules. They found that for strong electrolytes, even in dilute solutions, the fugacity, or activity, of the ions is not strictly proportional to the concentration, while that of the undissociated electrolyte is very far from proportional to its concentration.

[1] For a complete summary see Abegg-Auerbach and Luther, "Messungen elektromotorischer Kräfte."

[2] *Z. physik. Chem.*, **26**, 321 (1898).

[3] *Ibid.*, **33**, 545 (1900).

[4] THIS JOURNAL, **34**, 232 (1912).

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McInnes and Parker[1] have extended the electrometric measurement of the free energy of dilution to aqueous solutions of potassium chloride. Using silver chloride and amalgam electrodes, they determined the electromotive force of cells both with and without transference. From their data they were able to calculate the transport numbers and the activity ratios of the ions. They found that the concentration ratios calculated from conductivity are invariably higher than the activity ratios determined by the electromotive-force method; further, that the activity ratio approaches the value of the concentration ratio as the dilution increases.

Ferguson[2] also has worked with concentration cells containing hydrochloric acid, using electrodes reversible to both ions in cells with and without transference. He also found that the activity ratios are less than the concentration ratios.

Somewhat similar results were obtained by Ellis[3] for hydrochloric acid solutions in concentrations ranging from 0.00167 N to 4.484 N. Assuming provisionally that the activity coefficient of the most dilute solution is substantially equal to the ionization coefficient derived from the conductance ratio, he calculated a series of absolute activity coefficients for the remaining concentrations. Beginning with the most dilute solution, the activity coefficients, thus calculated, decrease with increasing concentration, pass through a minimum at 0.5 N and then increase with further increase in concentration. The conductance-viscosity ratio $\lambda\eta/\lambda_0\eta_0$ decreases throughout with increase in the concentration of the acid.

Thus far water has been the only solvent used in investigations of this nature. It was thought worth while therefore, to make a systematic comparative study of the influence of the solvent upon the electromotive forces, the transport numbers, the activity ratios of the ions and molecules, and the free energy of dilution of electrolytes in water and organic solvents.

The concentration cells chosen for this work consist of solutions of lithium chloride in water and in the five lower alcohols of the paraffin series.

In such a study it is necessary to make use of two types of concentration cells. Let us consider first the cell involving transference, *e. g.*,

$$\begin{array}{c|c|c|c} \text{Ag} & \text{AgCl, LiCl} & \text{LiCl, AgCl} & \text{Ag,} \\ & \xi'' & \xi' & (\xi'' > \xi') \end{array}$$

During the passage of one faraday of electricity, one equivalent of the chloride ion is formed on the dilute side from the silver chloride electrode, while on the concentrated side one equivalent of the chloride ion is removed from the solution to the electrode. At the same time N_c equivalents of the lithium ion migrate into the dilute chamber and $(1 - N_c)$ equivalents of the chloride ion migrate to the concentrated side. The total result is

[1] This Journal, 37, 1445 (1915).
[2] *J. Phys. Chem.*, 20, 326 (1916).
[3] This Journal, 38, 737 (1916).

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the transfer of N_c equivalents of lithium chloride from the concentrated to the dilute solution, or from the solution of activity ξ'' to that of ξ'. The free energy accompanying the transfer of one mole of the salt is given by the relation

$$-\Delta F = \frac{E.F}{N_c} = RT \log_e \frac{\xi''}{\xi'}, \qquad (1)$$

where E is the electromotive force, F the faraday (96494 coulombs), N_c the transport number of the cation, R the gas constant (8.316 j.), T the absolute temperature (298.09°).

The following cell does not involve transference:

$$\text{Ag} \left| \begin{matrix} \text{AgCl, LiCl} \\ \xi'' \end{matrix} \right| \begin{matrix} \text{LiCl (Li.Hg}_x\text{)} \\ \xi'' \end{matrix} - \begin{matrix} \text{(Li.Hg}_x\text{) LiCl} \\ \xi' \end{matrix} \left| \begin{matrix} \text{LiCl, AgCl} \\ \xi' \end{matrix} \right| \text{Ag}$$

The passage of one faraday of electricity involves, on the dilute side only, the formation of one equivalent of lithium chloride from the silver chloride and the amalgam electrodes. On the concentrated side there is transferred to the electrodes from the solution one equivalent of lithium chloride. The free energy accompanying this change is

$$-\Delta F_1 = E_1.F = RT \log_e \frac{\xi''}{\xi'}. \qquad (2)$$

Combining Equations 1 and 2 we arrive at an expression for calculating the transport number of the cation directly from electromotive-force measurements, *viz.*,

$$N_c = \frac{E}{E_1}. \qquad (3)$$

All cells on closed circuit tend to operate until the activities of the two solutions become equal. In cells without transference such an equalization by direct diffusion of the molecules and ions is impossible. The same result is obtained by the formation of the salt from the electrodes on the dilute side and the simultaneous removal of the salt to the electrodes on the concentrated side. It is obvious, therefore, that the free energy of dilution of lithium chloride is equal to the sums of the free energy of dilution of the separate ions, *i. e.*,

$$-\Delta F_1 = E_1.F = RT \log_e \frac{\xi''_{(LiCl)}}{\xi'_{(LiCl)}} = RT \log_e \frac{\xi''_{Li^+}.\xi''_{Cl^-}}{\xi'_{Li^+}.\xi'_{Cl^-}}.$$

Assuming that $\xi''_{Li^+} = \xi''_{Cl^-}$ and that $\xi'_{Li^+} = \xi'_{Cl^-}$, therefore the chloride ion

$$-\Delta F_1 = E_1.F = RT \log_e \frac{\xi''_{(LiCl)}}{\xi'_{(LiCl)}} = 2RT \log_e \frac{\xi''_{Cl^-}}{\xi'_{Cl^-}}. \qquad (4)$$

If this assumption is not true, and most probably it is not, then the calculated ratio of the activities of the chlorine ions may be taken as the ratio of the square roots of the products of the activities of the two ions.

The free energy of dilution in joules per gram-equivalent weight is equal

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to E_1, the electromotive force without transference, multiplied by the value of the faraday, or 96494 coulombs.

Materials and Apparatus.

The conductivity water used throughout the work was prepared according to the method of Jones and Mackay.[1]

Ethyl Alcohol.—Ordinary 95% alcohol was allowed to stand over fresh quicklime for three weeks; it was then decanted and distilled. The distillate was allowed to stand over anhydrous copper sulfate for one week and then redistilled. This distillate was refluxed over metallic calcium for ten hours and again distilled. To the last distillate were added a few crystals of pure dry silver nitrate and it was then refluxed for two hours to remove reducing agents. The distillate from this treatment was collected and preserved in dry glass-stoppered bottles, being protected from the air during distillation by a drying train containing fused calcium chloride. In each distillation a fractionating column was used and only that middle portion passing over between 77.9° and 78° (uncorr.) was retained.

The remaining alcohols, *viz.*, methyl, *n*-propyl, *n*-butyl and isoamyl, were of Kahlbaum's best grade. These were further purified in the same manner as was the ethyl alcohol, except that the treatment with quicklime was omitted. The uncorrected distillation temperatures were: methyl, 64.9–65.1°; *n*-propyl, 95.7–95.9°; *n*-butyl, 115.8–116.2°; isoamyl, 129.9–130.2°.

Lithium Chloride.—Kahlbaum's best grade of lithium chloride was recrystallized four times by passing pure hydrogen chloride into a hot saturated solution of the salt in conductivity water. The crystals were filtered on a Büchner funnel and sucked dry. They were then heated in a platinum dish in an electric oven in which the temperature was gradually raised to 150°. The dry salt was then finely powdered in a hot agate mortar and transferred to porcelain boats. These were placed in a combustion tube and heated for several hours at 160° in a rapid stream of dry hydrogen chloride. All traces of the latter were removed by a stream of dry hydrogen, after which the boats were allowed to slide quickly into large glass-stoppered weighing tubes.

Solutions.—All of the solutions were prepared by first dissolving an amount of the salt in excess of that required for the highest concentration. The chloride content was then determined in at least four separate samples by the Drechsel[2] modification of the Volhard method. All of the various concentrations in any given solvent were made by the proper dilution of this mother solution, the greatest care being taken to secure the least possible contact with the air. All of the measuring apparatus was certified and the solutions were made up to volume at 25°.

[1] *Am. Chem. J.*, **19**, 83 (1897).

[2] *Z. anal. Chem.*, **16**, 351 (1877).

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Mercury.—The mercury used was repeatedly washed by spraying through dilute nitric acid, and then further purified by distilling in a current of air under reduced pressure.

Lithium Amalgam.—This was prepared by the electrolysis of a saturated solution of the salt in pyridine, using pure redistilled mercury as the cathode. It was then washed with absolute alcohol, quickly dried by gentle heating under reduced pressure (Gaede pump), then filtered through a fine capillary tube into a sealed glass container from which the air had previously been displaced by dry hydrogen.

Electrodes.—The silver chloride electrodes consisted of short, thick pieces of pure silver wire fused into the ends of glass tubes. To the ends within the tubes were soldered long copper wires which were of such length that they could be bent into small mercury cups, thus making contact with the wire leads. Twelve or fifteen of the electrodes thus prepared were first grouped as cathodes about a single pure silver anode immersed in a solution of potassium-silver-cyanide. After a dense white coating of silver had been formed they were removed, rinsed and then inserted as anodes in a 1.0 *N* hydrochloric acid. On passing a current from a single accumulator for one to two minutes there is formed a closely adhering reddish brown deposit of silver chloride. For any one series of measurements the chloride electrodes were always first checked against each other. This was done by grouping them in a dilute solution of hydrochloric acid and observing the potential difference between each electrode and another taken as standard. Only those varying by less than 0.05 mv. were chosen. Three of these electrodes were placed in each half cell. After they had been in contact with each other for four or five hours the potential readings were taken. In taking these readings the electrodes in each half-cell were first checked against each other. Unless at least two electrodes differed by less than 0.02 mv., the cell was disconnected and the electrodes replated. When the potential deviations proved to be within these limits the potentials were read between each single electrode of one cell and the separate electrodes of the other cell and the mean value taken. For a further check the electrodes in each half cell were connected and the electromotive force between the combined electrodes was then determined.

The form of cell adopted was such that concentration cells, both with and without transference, could be obtained from a single set-up of the apparatus. Two half-cells of the form used by Ferguson,[1] each having two side tubes and containing solutions of the desired concentrations in contact with the chloride electrodes, were so arranged that from one set of side tubes a liquid junction could be made and the electromotive force with transference thus obtained. The other set of tubes were thus left

[1] *Loc. cit.*

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free for liquid connection with small cells into which dipped the amalgam electrodes, thus forming the cell without transference.

Liquid connection between the half cells was effected by means of an inverted T-tube fitted with a three-way stopcock. To minimize diffusion loose plugs of cotton were inserted into the bore of these stopcocks. For cells with transference it is very essential that a sharp boundary be produced between the solutions immediately before measurements are taken. Fresh contacts were readily made by drawing more of each solution into the free limb of the T-tube. It was found that the electromotive forces of cells directly connected remained constant for several days when this precaution was observed.

The amalgam electrodes were similar to those used by MacInnes and Parker;[1] the method of procedure was also the same. As a result of numerous experiments, a concentration of 0.002 % was found to give the best results. It was found that by dropping from 20 to 30 drops per minute no appreciable bubbling occurred and the voltage remained very constant for several minutes. Occasionally, the galvanometer would waver slightly but it would immediately return to zero upon the formation of another drop of the amalgam.

All measurements of the electromotive force were made with a Wolff potentiometer in connection with a sensitive Leeds and Northrup, "Type H," wall galvanometer. A Cadmium-Weston cell which had been recently standardized and frequently rechecked against a similar element, also recently standardized by the Bureau of Standards, was used as the standard of reference. Although its temperature coefficient is practically negligible, this cell was kept in an insulated glass beaker suspended in the constant temperature bath. All measurements were made at 25° ±0.01°.

Precision and Duplication of Results.

The resistance of the solutions increases with increasing molecular weight of the solvent; obviously, the precision to be obtained decreases somewhat accordingly. However, it was not found difficult to duplicate potentiometer readings for any pair of concentrations in any of the solvents used.

Quadruplicate determinations of the electromotive force were made for all pairs of concentrations in water, methyl alcohol and ethyl alcohol. This involved four distinctly different set-ups of the apparatus, including new solutions and three freshly plated concordant electrodes for each half cell. The results recorded represent, therefore, the mean of four "mean" potential differences which, over all, do not differ by more than 0.05 mv.

The electromotive forces recorded for solutions in *n*-propyl and isoamyl alcohols are the mean of duplicate measurements, made as previously described. This was deemed sufficient, since the potentiometer readings checked exactly to the last significant figure. The supply of *n*-butyl

[1] *Loc. cit.*

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alcohol at our disposal permitted but a single determination of the electromotive force for a single pair of concentrations in this solvent. Since, however, each half cell contained three electrodes which checked over all to 0.02 mv., and since each electrode was measured directly against each of the three electrodes in the opposite cell, the results obtained for this solvent may be considered as the mean of six different determinations for the same pair of solutions.

Discussion.

Lithium chloride was chosen as the electrolyte because of its relatively high solubility in all of the solvents under consideration. Its use is hampered, however, by certain disadvantages. Various lines of evidence point to its inherent tendency to polymerize when dissolved in the alcohols and other organic solvents,[1] and also to the tendency of both the molecules and the ions to form complex solvates with the solvents.[2] Washburn and MacInnes[3] have calculated for a 0.5 N aqueous solution of lithium chloride a probable hydration of 18 moles of water to one mole of the salt.

For a given temperature, the complexity of these solvates must increase with increase in the proportion of the solvent. When the phenomenon of association is present, it is very probable also that both the polymerized molecules and their ions are solvated to some extent. For any given concentration of the salt in any one of the solvents, except perhaps water, we must take into consideration the possible existence of an equilibrium not only between the solvated simple and complex molecules, but also between the two molecular species and their solvated ions, *e. g.*,

$$\mathrm{Li^+}.S_1+\mathrm{Cl^-}.S_2 \rightleftarrows \mathrm{LiCl}.S_3 \rightleftarrows (\mathrm{LiCl})_2.S_4 \begin{cases} \rightleftarrows \mathrm{Li^+}.S_1+\mathrm{LiCl^-}_2.S_5 \quad (a) \\ \text{or} \\ \rightleftarrows \mathrm{Li_2Cl^+}.S_6+\mathrm{Cl^-}.S_3 \quad (b) \end{cases} \qquad (5)$$

where S_1, S_2, S_3, etc., represent the number of moles of combined solvent.

Slight association, if any, should be expected in water, methyl alcohol and ethyl alcohol. For the alcohols, the relative degree of association of the salt should increase with the decrease in the dissociating power of the solvent, or, as in the present work, with an increase in the molecular weight of the alcohols.

An increase in the concentration of the salt will tend to displace the above equilibrium toward the right. With an increase in the concentration of the polymerized salt molecules there is very probably associated also an increase in the formation of complex ions of greater electro-affinity.[4]

[1] Andrews and Ende, *Z. phys. Chem.*, 17, 136 (1905).

[2] Jones and Getman, *Ibid.*, 46, 261 (1903); *Am. Chem. J.*, 32, 338 (1904); Jones and McMaster, *Ibid.*, 35, 445 (1906).

[3] THIS JOURNAL, 33, 1705 (1911).

[4] Sachanov, *J. Russ. Phys. Chem. Soc.*, 44, 324 (1912); Pearce, *J. Phys. Chem.*, 19, 14 (1915).

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On the other hand, a sufficient decrease in the concentration will naturally result in the formation of the solvated simple molecules and their ions. While the magnitude of the solvation per mole of the solute decreases with increase in concentration, the total amount of solvent removed from action as combined solvent will be greater, the greater the concentration of the salt. With a decrease in the amount of effective solvent, due to solvation, there is an abnormal increase in the actual concentration of the solute particles, and very probably, therefore, a corresponding abnormal increase in the activity of both the molecules and the ions, whether simple or complex. It is obvious therefore that for such equilibria as that represented above we should expect anomalous relations to appear as we pass from very dilute to very concentrated solutions.

Changes in the extent of polymerization, in ion complexity and in solvation with change in concentration must abnormally effect the electromotive forces of cells without transference. These changes together with the accompanying changes in viscosity must also affect the mobilities of the ions and, therefore, the electromotive forces of cells with transference.

Solvation and polymerization of the salt are not the only factors involved in the study of solutions of electrolytes in organic solvents. The activity of the dissolved molecules and ions is a function of their concentration. According to the Nernst-Thomson rule, the dissociating power of the solvent will be greater, the greater is its dielectric constant. Consequently, considering a given concentration of the electrolyte in various solvents, that solution will contain the greatest concentration of ions, and hence the greatest ion activity, whose solvent possesses the highest dielectric constant.

Euler[1] has found that the dielectric constants of solutions increase with their ion concentration. In some work carried out in this laboratory several years ago[2] it was found that the dielectric constant of solutions of silver nitrate in methyl and ethyl alcohol increases linearly with the concentration up to 0.05 N.

Walden[3] has found that the dielectric constants of solvents of feeble ionizing power are increased by dissolving in them certain binary salt. The increase in the value of the constant is dependent upon the constitution of the salt. Strong salts, *e. g.*, lithium chloride, when dissolved possess high dielectric constants and exhibit a great tendency to ionize. The degree of ionization of the salt depends both on the dissociating power of the solvent and the ionizing tendency of the salt. As both of these factors increase with the dielectric constant the highest degree of ionization—hence of ion concentration and ion activity for a given concentration of

[1] *Z. phys. Chem.*, **28**, 619 (1899).

[2] Unpublished.

[3] THIS JOURNAL, 35, 649 (1913).

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the salt,—will be found in a system where both the solvent and the solute possess large dielectric constants.

TABLE I.—ELECTROMOTIVE FORCES WITH TRANSFERENCE (VOLTS).

Solvent.	Concentration ratios (10 : 1). 1.0–0.1.	0.5–0.05.	0.1–0.01.	0.05–0.005.
Water	0.03194	0.03503	0.03583	0.03640
Methyl alc.	...	0.03857	0.04004	0.04104
Ethyl alc.	...	0.03323	0.03560	0.03820
n-Propyl alc.	...	0.02817	0.02845	0.0311
n-Butyl alc.	0.02740	0.0271	0.0242	0.0250
Isoamyl alc.	0.02630	0.0255	0.0243	0.0240

For solutions in water, methyl, ethyl, and propyl alcohols the electromotive forces with transference increase regularly with increase in dilution. Normally this is just what we should expect. In the *n*-butyl alcohol the electromotive force first decreases, passes through a minimum and then increases slightly upon further dilution. For the isoamyl alcohol there is a corresponding decrease in the values of the electromotive force, tending toward a minimum in the most dilute pair.

TABLE II.—ELECTROMOTIVE FORCES WITHOUT TRANSFERENCE (VOLTS).

Solvent.	Concentration ratios (10 : 1). 1.0–0.1.	0.5–0.05.	0.1–0.01.	0.05–0.005.
Water	0.11433	0.10868	0.10433	0.09957
Methyl alc.	...	0.09387	0.07978	0.07162
Ethyl alc.	...	0.08875	0.07170	0.06143
n-Propyl alc.	...	0.07885	0.05890	0.0575
n-Butyl alc.	0.0825	0.0772	0.0579	0.0501
Isoamyl alc.	0.0701	0.0625	0.0535	0.0430

For cells without transference the electromotive force of all pairs in the same solvent decreases with increase in dilution. This is exactly the opposite of what we should expect; for, with a normality ratio of 10 : 1, it would be expected that the concentration ratios, as well as the activity ratios, of the ions should gradually increase to the value of 10 at infinite dilution. It is evident that lithium chloride behaves abnormally in all of these solvents. A discussion of this abnormality will be taken up later.

Using the conductivity data of Greene[1] for solutions of lithium chloride in water and those of Jones and Turner[2] for solutions in ethyl alcohol, we calculated the electromotive forces for cells both with and without transference. In both solvents the calculated values increase with increasing dilution, but in neither type of cell does the Nernst equation apply even approximately.

The transference number of the lithium ion increases with increase in dilution in each of the solvents studied. For a given change in the dilution

[1] *Trans. Chem. Soc.*, 93, 2042 (1908).

[2] *Am. Chem. J.*, 40, 558 (1908).

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this increase is least in the aqueous and greatest in the ethyl alcohol. Except for the most dilute cell in the ethyl alcohol, the highest values for the transference number are obtained for solutions in methyl alcohol. For similar concentrations in the alcohols the transference number decreases with increase in the molecular weight of the solvent until isoamyl alcohol is reached, where the corresponding values are found to increase.

TABLE III.—TRANSFERENCE NUMBERS OF THE LITHIUM ION.

	Concentration ratios (10 : 1).			
Solvent.	1.0–0.1.	0.5–0.05.	0.1–0.01.	0.05–0.005.
Water	0.279	0.322	0.343	0.365
Methyl alc.	...	0.411	0.502	0.573
Ethyl alc.	...	0.374	0.497	0.622
n-Propyl alc.	...	0.357	0.483	0.541
n-Butyl alc.	0.332	0.351	0.418	0.499
Isoamyl alc.	0.375	0.408	0.454	0.555

When the concentration is such that the possibility of the presence of complex ions exists, the transference number obtained for an ion, *e. g.*, the anion, will be the sum of the transference numbers of the simple and complex anions present. Only at sufficiently high dilutions will we obtain the transference number of the simple ion.

The values for the transference numbers obtained by the electromotive-force method are the mean values between the two concentrations constituting the cell. It is therefore difficult to make a comparison with data directly determined. Table IV gives the values determined by Kohlrausch and Holborn[1] for the transference number of the lithium ion in aqueous solutions at 25°. The mean values have been calculated and are inserted for comparison.

TABLE IV.—COMPARISON OF THE TRANSFERENCE NUMBERS OF THE LITHIUM ION.

	1.0–0.1		0.5–0.05.		0.1–0.01.		0.05–0.005.	
Kohlrausch	0.261	0.310	0.270	0.330	0.310	0.370	0.330	0.390[2]
Mean N_c (K)	0.285		0.300		0.340		0.360	
Mean N_c (e. m. f.)	0.279		0.322		0.343		0.365	

The agreement is as satisfactory as could be expected and it confirms the applicability of this method of determining transference numbers.

TABLE V.—FREE ENERGY OF DILUTION (JOULES).

	Concentration ratios (10 : 1).			
Solvent.	1.0–0.1.	0.5–0.05.	0.1–0.01.	0.05–0.005.
Water	11032	10487	10067	9608
Methyl alc.	...	9205	7698	6911
Ethyl alc.	...	8564	6919	5928
n-Propyl alc.	...	7608	5684	5548
n-Butyl alc.	7961	7450	5587	4834
Isoamyl alc.	6764	6031	5162	4149

[1] "Leitvermögen der Elektrolyte," p. 201.

[2] Extrapolated.

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It will be observed that for a given normality ratio (10 : 1) the free energy of dilution of lithium chloride decreases regularly as we pass from the lower to the higher members of the same homologous series. Furthermore, for any one of the solvents studied the free energy decreases as the pair of concentrations involved become more dilute. Since the free energy of dilution is proportional to the logarithm of the ratio of the activities of the chlorine ions, we should expect, for the normality ratio used, that the free energy would increase to a maximum at infinite dilution.

Table VI gives a summary of the activity ratios of the ions as calculated by a simple rearrangement of Equation 4. This ratio in the various solvents decreases with increase in dilution of the pairs constituting the cells, and this in spite of an increase in the normal ionization of the electrolyte. A similar decrease was observed by Noyes and Ellis[1] for concentrated solutions of hydrochloric acid. For concentrations ranging from 4.484 N to 0.5 N they found a decrease in the activity ratios with dilution, followed by an increase in the value of the ratio with further dilution between 0.5 N and 0.00338 N.

TABLE VI.—ACTIVITY RATIOS OF THE IONS.

	Concentration ratios (10 : 1).			
Solvent.	*A.* 1.0–0.1.	*B.* 0.5–0.05.	*C.* 0.1–0.01.	*D.* 0.05–0.005.
Water	9.254	8.285	7.617	6.942
Methyl alc.	...	6.215	4.725	4.031
Ethyl alc.	...	5.626	4.037	3.305
n-Propyl alc.	...	4.640	3.147	3.062
n-Butyl alc.	4.981	4.493	3.086	2.651
Isoamyl alc.	3.913	3.375	2.833	2.309

The relative effect due to an increase in the concentration of the lithium chloride by two-, five-, ten-, and twentyfold upon the activity ratios is shown in Table VII, where A/B, C/D, etc., represent the ratio of the activity of the ions for one pair of concentrations (A) to that of another pair (B), etc. These values point distinctly to an increase in ionic activity with increase in concentration of the dissolved salt. As might be expected, this increase is least in the aqueous solutions and it increases as we pass upward in the series of the alcohols.

TABLE VII.—COMPARATIVE EFFECT OF CONCENTRATION UPON THE ACTIVITY RATIOS.

Solvent.	*A/B* 2-fold.	*C/D* 2-fold.	*B/C* 5-fold.	*A/C* 10-fold.	*B/D* 10-fold.	*A/D* 20-fold.
Water	1.17	1.09	1.09	1.21	1.19	1.33
Methyl alc.	..	1.17	1.31	..	1.54	..
Ethyl alc.	..	1.22	1.39	..	1.70	..
Propyl alc.	..	1.03	1.47	..	1.51	..
Butyl alc.	1.11	1.16	1.45	1.61	1.69	1.88
Isoamyl alc.	1.16	1.22	1.19	1.38	1.46	1.69

[1] THIS JOURNAL, 39, 2543 (1917).

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In the earlier part of the discussion three factors were discussed, one or more of which may affect the activity ratios of the ions. These were the effect of hydration, the effect of polymerization of the solute molecules followed by complex ionization and the effect of change in the dielectric constant of the solution with change in concentration.

Lithium chloride and more especially the lithium ion exhibit a marked tendency to form complex hydrates in aqueous solution. Similar solvates are to be expected in the various alcoholic solutions.

For a salt which does not form solvates the degree of ionization, and, hence, both the concentration and the activity of the ions, normally decrease with increase in concentration. For salts which tend to form solvates, the total amount of solvent removed from the solution by solvation increases with increase in the concentration of the salt, thus increasing somewhat abnormally both the concentration and the activity of the ions for any given concentration.

Considering any pair of concentrations constituting the cell and using a normality ratio (10 : 1), this abnormal effect will be greater in the more concentrated solution and the abnormality will become relatively greater as the concentration of each of the solutions is proportionally increased. For this reason the ratio of the activities of the ions should *tend* to increase with increase in concentration. At sufficiently high dilutions, on the other hand, the effect due to solvation becomes a minimum and the amount of combined solvent is negligibly small compared with that actually present as solvent. Hence, increase in dilution should be accompanied by a normal increase in the concentration and activity ratios.

The force tending to bring about the recombination of two oppositely charged ions is given by the well-known relation of Coulomb $f = e.e^1/K.d^2$. Or, if we assume the Nernst-Thomson rule, for a given concentration of the electrolyte in the various solvents, the degree of ionization, likewise the concentration and the activity of the ions, increases with the dielectric constant of the solvent.

Table VIII shows the relation between the activity ratios of the ions and the dielectric constant of the solvent.

TABLE VIII.—RELATION BETWEEN ION ACTIVITY RATIOS AND DIELECTRIC CONSTANTS.[1]

	H_2O.	CH_3OH.	C_2H_5OH.	C_3H_7OH.	C_4H_9OH.	$C_5H_{11}OH$.
K_d	80.0	32.2	26.1	22.0	19.0	16.0
$\sqrt{K_d}$	8.94	5.67	5.108	4.69	4.356	4.0
$A/\sqrt{K_d}$	1.03	...	..	...	1.14	0.98
$B/\sqrt{K_d}$	0.92	0.91	0.91	0.98	0.97	0.84
$C/\sqrt{K_d}$	0.85	0.83	0.79	0.67	0.71	0.71
$D/\sqrt{K_d}$	0.72	0.71	0.65	0.65	0.61	0.58

where K_d represents the dielectric constant of the solvent and A, B, C, D represent the activity ratios of the ions taken from Table VI.

[1] Nernst, "Theoretical Chemistry," Trans., 7th Ger. ed., p. 345.

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These data point unmistakably to the existence of a definite relation between the activity ratios and the dielectric constants. Considering first the dilute solutions, it will be observed that the ratio$(\xi''/\xi')/\sqrt{K_d}$, does increase with increase in the dielectric constant. For all solvents this ratio increases with increase in the concentration of the solutions constituting the cells and at sufficiently high concentrations approaches equal values for all solvents. The striking equality of this ratio for different concentration ratios in water and methyl alcohol is significant.

Hence, for sufficiently high equivalent concentrations of lithium chloride in water and the paraffin alcohols, we may state that the activity ratios of the ions in equivalent concentration ratios (10 : 1) are approximately proportional to the square roots of the dielectric constants of the solvents, or perhaps better still of the solutions. Unfortunately, we do not know the dielectric constants of any of these solutions.

Since the activity ratios of the ions increase both with the concentration and with the dielectric constant, the activity of the ions in a given solution will be greater, the greater both the concentration and the dielectric constant. There is, therefore, an apparently direct relation between the activity of the ions and their electro-affinities.[1]

Smale[2] has studied the effect of various electrolytes upon the dielectric constant of water. Two of these have an important bearing upon this work. The results are expressed in terms of the dielectric constant of water taken as unity.

Salt...	Conc.	0.001	0.002	0.005	0.008	0.010	0.030
KCl...	K =	1.013	1.018	1.034	1.070	1.113	1.160
HCl...	K =	0.990	1.033	1.064	1.090	1.126	...

Neither potassium chloride nor its ions exhibit any appreciable hydrating power. Hydrogen chloride, on the other hand, shows a marked affinity for water. Both increase the dielectric constant of water. The decrease in the activity ratios of the ions of potassium chloride (MacInnes and Parker) and the increase in the activity ratios of the ions of hydrochloric acid (Noyes and Ellis), both with increase in concentration, may in all probability be due entirely to differences in hydrating power. The activity ratios of the ions should increase with the concentration most rapidly for salts which have high dielectric constants and great hydrating power.

It is obvious, therefore, that changes in the free energy of dilution, of electromotive force and other factors depending upon the activity ratios must be intimately related to changes in the dielectric constants of the solutions.

While the effects due to solvation and changes in dielectric constant may

[1] By electro-affinity is meant the power of a cation to repel, or the power of an anion to attract an electron.

[2] *Ann. Phys. Chem.*, [ii] 61, 625 (1897).

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explain in part the increase in the activity ratios for solutions in water and the lower alcohols, they alone will not suffice for the interpretation of the effects observed in the higher alcohols. In the latter we undoubtedly have present not only the simple molecules and simple ions, but also polymerized molecules and complex ions, all in equilibrium as represented in (5*a*) or (5*b*). A continuous increase in the concentration of the salt results in a constantly increasing concentration of one of the complex ions, *e. g.*, $LiCl_2^-.S_5$, or $Li_2Cl^+.S_6$. There is also a corresponding increase in the number of the oppositely charged simple ion. The activity ratio of the negative or positive ions now involves the activities of both the simple and complex ions of each.

For any concentration ratio (10 : 1) the effect produced by polymerization will always be greater in the more concentrated solution and it will increase relatively the more rapidly the greater the proportional increase in the concentration of the two solutions constituting the cell. The abnormal increase in the concentration of the complex ions, coupled with an increase in the dielectric constant and with an increase in the total amount of combined solvent, with increase in concentration of the salt, should and do increase the activity ratios of the ions.

TABLE IX.—ACTIVITY RATIOS OF THE MOLECULES.

	Concentration ratios (10 : 1).			
Solvent.	1.0–0.1.	0.5–0.05.	0.1–0.01.	0.05–0.005.
Water	85.63	68.64	58.02	48.19
Methyl alc.	...	38.63	22.33	16.25
Ethyl alc.	...	31.65	16.30	13.75
n-Propyl alc.	...	21.53	9.90	9.37
n-Butyl alc.	24.81	20.19	9.52	7.03
Isoamyl alc.	15.31	11.39	8.03	5.30

The effect of solvent and concentration upon the ratio of the molecules is shown in Table IX. From the relation presented in Equation 4 these ratios are equal to the square of the corresponding activity ratios of the ions. Factors influencing the latter will also influence these accordingly. These data require no further discussion.

This work is being continued with other salts.

Summary.

The electromotive forces of concentration cells have been determined for solutions of lithium chloride in water, methyl, ethyl, *n*-propyl, *n*-butyl and isoamyl alcohols. All of the cells measured contained solutions having a normality ratio of 10 : 1.

The electromotive force with transference increases with increasing dilution for all of the solvents used, except butyl and isoamyl alcohols in which it decreases. The electromotive force without transference decreases with increases in dilution in all of the solvents.

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The transport number of the lithium ion has been calculated and it has been found to increase in each solvent as the concentration of the salt is diminished.

The free energy of dilution and the activity ratios of both the ions and the molecules, on the other hand, decrease with the dilution.

An attempt has been made to explain the decrease in the activity ratios, and hence the free energy, on the assumption of effects due to hydration and the change in dielectric constant. For the higher alcohols, it has been found necessary to assume a polymerization and subsequent complex ionization of the salt molecules.

For a given pair of concentrations the activity ratios of the ions increase with increase in the dielectric constant of the solvent. The ratio $(\xi''/\xi')/\sqrt{K_d}$ increases with increase in concentration and at the same sufficiently high equivalent concentrations attains an approximately equal value for all solvents. For these concentrations the ration (ξ''/ξ') is very nearly directly proportional to the square root of the dielectric constant of the solvent. For similar cells in water and methyl alcohol these ratios are practically identical.

The activity of the ions has been found to increase both with the concentration and with the dielectric constant of the solvent, or of the solution.

IOWA CITY, IOWA.

THE NATURE OF THE INOSITE PHOSPHORIC ACIDS OF SOME IMPORTANT FEEDING MATERIALS.[1]

BY J. B. RATHER.

Received December 6, 1917.

The theory that phytic acid, an inosite phosphoric acid found in seeds of plants as a complex salt known as phytin, corresponds in composition to the formula $C_2H_8P_2O_9$ was first proposed by Posternak.[2] Much of the work of European investigators does not agree with this view. Investigations made in America by Patten and Hart[3] and Hart and Tottingham[4] and the earlier work of Anderson[5] gave results in accord with the theory of Posternak. It was found by the present writer however, that cottonseed meal and wheat bran yielded an inosite phosphoric acid richer in carbon and poorer in phosphorus than is required for the formula proposed by

[1] That portion of this work relating to corn and kafir corn and a part of that relating to wheat bran was read before the American Chemical Society in Kansas City, April, 1917.

[2] *Rev. Gen. Bot.*, 12, 5 and 65; *Compt. rend.*, 137, 35–8.

[3] N. Y. (Geneva) Expt. Sta., *Bull.* 250.

[4] Wisconsin Expt. Sta., *Tech. Bull.* 9.

[5] N. Y. (Geneva) Expt. Sta., *Tech. Bulls.* 19 and 21.

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Posternak.[1] Anderson[2] believed that "cottonseed meal contains an organic phosphoric acid very similar to phytic acid," and that wheat bran[3] contains an inosite phosphoric acid of the formula $C_{25}H_{65}P_9O_{54}$ containing pentose in the molecule, and which decomposes into an inosite phosphoric acid of the formula $C_{20}H_{55}P_9O_{49}$ with the loss of the pentose group. The examination of wheat bran made by Patten and Hart, which preceded that of other workers, led them to conclude that the acid corresponded in composition to the phytic acid of Posternak, namely, $C_2H_8P_2O_9$. The present writer concluded[4] that the acid corresponded in composition to the formula $C_{12}H_{41}O_{42}P_9$ and showed that Anderson's pentose theory was based on inadequate evidence. Later Anderson repeated his work and at first concluded[5] that wheat bran contains a number of inosite phosphoric acids, and later[6] that wheat bran contains inosite monophosphate, inosite triphosphoric acid and inosite hexaphosphoric acid, and also that cottonseed meal contains inosite hexaphosphoric acid.[7] He does not appear to repeat his claim that wheat bran contains an inosite pentose phosphoric acid. Boutwell[8] was unable to obtain the inosite monophosphate from wheat by Anderson's method, nor was he able to separate the inosite hexaphosphoric acid claimed to be present by Anderson. Boutwell's products failed to correspond in composition to that of any simple phosphoric acid ester of inosite.

Anderson has criticised the method of preparation used by the present writer and claims that products so prepared are impure, and in the case of wheat bran highly contaminated with orthophosphoric acid. It has recently been shown however[9] that an entirely different method of preparation yields the same results on cottonseed meal, and that cottonseed meal contains an inosite phosphoric acid corresponding in composition equally as well to the formula $C_{12}H_{41}O_{42}P_9$ previously proposed and to the formula $C_6H_6(OH)(H_2PO_4)_5$, inosite pentaphosphoric acid. The first formula divided by 2 gives figures essentially the same as the latter formula, and since the latter is that of a theoretically possible compound it was adopted as the more desirable. These products, as was with the case criticised by Anderson, were shown to be free from inorganic bases, orthophosphoric acid and other impurities.

[1] Rather, THIS JOURNAL, 35, 890 (1913).
[2] N. Y. (Geneva) Expt. Sta., *Tech. Bull.* 25.
[3] *Ibid.*, 22.
[4] *Loc. cit.*
[5] *J. Biol. Chem.*, 18, 425 (1914).
[6] *Ibid.*, 18, 441 (1914); *Ibid.*, 20, 463 (1915); N. Y. (Geneva), *Tech. Bull.* 40, 25.
[7] *J. Biol. Chem.*, 17, 141 (1914).
[8] THIS JOURNAL, 39, 491 (1917).
[9] Rather, *Ibid.*, 39, 777 (1917).

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The work described below is a continuation of the study of the nature of the inosite phosphoric acids of feeding materials.

Experimental.

The method of separation and purification of the inosite phosphoric acid of feeding materials has considerable effect on the composition. It is not only necessary to separate the acid from inorganic bases, but to avoid hydrolysis by enzymes or other agencies, to separate it from other acids, known and unknown, which occur in the material under examination, and to prepare a compound which can be purified and demonstrated to be pure. These requirements have not always been observed.

The method of preparation adopted in the present work consists of removing the inorganic bases from the crude acid with alcohol, and fractionating the material by means of the strychnine salt. The process has been shown[1] to free the acid from inorganic bases, orthophosphoric acid, oxalic, hydrochloric and acetic acid and from other compounds of an unknown nature. Numerous experiments indicated that the effect of enzymes during the time of extraction has no effect on the composition of the principal product of the procedure. The strychnine salt can be fractionated by recrystallization to any desired extent and the purity of the material demonstrated by uniformity in composition and melting points of the several fractions. The method briefly is as follows:

Digest the finely ground material with 0.2% hydrochloric acid for 3 hours with frequent stirring. Filter through two layers of closely woven cloth, pouring back until the filtrate comes through clear. Add immediately copper acetate solution in excess, filter the copper precipitate and wash with water. Decompose the copper salt with hydrogen sulfide, filter and evaporate to a small volume at 55–60° under a strong current of air. Take up with 6 volumes of 95% alcohol and filter off the insoluble matter. Dissolve the insoluble matter, consisting of acid salts, in acidulated water, precipitate with copper acetate solution and complete as before. This process should be repeated again on any insoluble residue remaining. Evaporate the combined alcohol solutions to a syrup at 50° under a strong current of air, take up again in alcohol, filter if necessary, and evaporate as before. This process removes all inorganic bases. The inosite phosphoric acid is then separated and purified as follows: Weigh the crude acid, dissolve in about three liters of water, filter off the insoluble matter, if any, add to the warm solution an amount of reprecipitated strychnine equal in weight to the syrupy acid. It is necessary to use this ratio of strychnine to acid in order to get a salt of the inosite phosphoric acid which will not give equivocal results on analysis.[1] All of the strychnine should go into solution. Filter if necessary, and concentrate at 55–60° under a strong current of air until crystals begin to form. Then allow to

[1] Rather, THIS JOURNAL, 39, 777 (1917).

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cool. Filter and concentrate the mother liquor as above until crystals begin to appear, cool, filter and concentrate the mother liquor again. Purify the fractions by recrystallization in the usual manner. This process separates the inosite phosphoric acid from orthophosphoric acid, oxalic acid and other acids.

The material which is crystallizable consists almost entirely of the inosite phosphoric acid described below.

The Occurrence of Inosite Pentaphosphoric Acid in Wheat Bran.—The material was prepared as described above. 5 kg. of ground wheat bran and 40 liters of 0.2% hydrochloric acid were used. One hundred grams of the crude acid were obtained and from this 65 g. of a strychnine salt melting at 220–22° (uncorr.). Other crystalline and non-crystalline phosphorus-bearing materials were found.

The fraction melting at 220–2° consisted of large scales made up of microscopic needles and plates. It was recrystallized from water without change in melting point. It was then fractionated into two portions without change in melting point. The mother liquor from the second fraction yielded crystals which gave the same melting point.

The two fractions were analyzed after drying at 105° in a vacuum over phosphorus pentoxide. They remained unchanged in color upon drying. They were free from bases other than strychnine and from orthophosphoric acid. Nitrogen was determined by the Kjeldahl method, phosphorus by the official volumetric method, after destroying the organic matter by ignition with magnesium nitrate, and carbon and hydrogen by combustion in a current of oxygen, the material being mixed in the boat with fine copper oxide. The results follow:

Calc. for the octastrychnine salt of the acid $C_{12}H_{41}O_{42}P_9$: C, 56.72; H, 5.70; N, 5.88; P, 7.33.

Calc. for tetrastrychnine inosite pentaphosphate, $C_6H_6(OH)(H_2PO_4)_5(C_{21}H_{22}N_2O_2)_4$: C, 56.33; H, 5.48; N, 5.84; P, 8.09.

Found, Fraction 1: C, 56.32, 56.39; H, 5.09, 5.22; N, 5.44; P, 7.89.

Found, Fraction 2: C, 56.18; H, 5.20; N, 5.30; P, 7.45.

The products correspond in composition to the octastrychnine salt of the acid $C_{12}H_{41}O_{42}P_9$, the formula for the acid of wheat bran previously proposed by the writer. They also correspond equally as well in composition to tetrastrychnine inosite pentaphosphate. No other salt of any simple ester of inosite and phosphoric acid has a similar composition. The facts that the melting point of the material remained unchanged upon recrystallization, that different fractions have the same composition, is considered sufficient evidence of the purity of the salt. The writer has shown in a previous publication[1] that under the conditions of the method of preparation there is no formation of a strychnine salt of the inosite

[1] THIS JOURNAL, 39, 777 (1917).

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phosphoric acid which has a similar composition to the salts of lower or higher esters of phosphoric acid and inosite.

Earlier work of the writer has shown that the analysis of the acid in a free state gives misleading results. This is also the present opinion of other workers in this field. Boutwell[1] has shown that the inosite phosphoric acid of wheat bran decomposes on mere drying *in vacuo* over phosphorus pentoxide at room temperature. For these reasons the silver salt was prepared and analyzed instead of the free acid.

Three g. of the purified strychnine salt were dissolved in water with the aid of heat, the strychnine precipitated with a slight excess of ammonia, the mixture cooled rapidly and the strychnine filtered off. The filtrate was washed with ether and boiled until the slight excess of ammonia was expelled. Three g. of silver nitrate in solution were added to the hot solution of the ammonium salt and the resulting silver salt was filtered off and washed with water. It was dried *in vacuo* over phosphorus pentoxide at 100°. Whenever protected from light there was only a slight change in color. The analytical results follow:

Calc. for $C_{12}H_{25}O_{42}P_9Ag_{16}$: C, 5.06; H, 0.88; P, 9.81; Ag, 60.66.

Calc. for nonasilver inosite pentaphosphate, $C_6H_6(OH)H(PO_4)_5Ag_9$: C, 4.67; H, 0.52; P, 10.05; Ag, 62.96.

Found, Fraction 1: C, 4.94; H, 0.97; P, 9.77; Ag, 61.77.

Found, Fraction 2: C, 4.89; H, 1.05; P, 9.95; Ag, 62.04.

Calc. for inosite pentaphosphoric acid, $C_6H_6(OH)(H_2PO_4)_5$: C, 12.41; P, 26.72.

Composition of free acid calc. from composition of Ag salt:

Fraction 1: C, 12.80; P, 26.26.

Fraction 2: C, 12.69; P, 25.82.

The free acid was prepared from the strychnine salt by means of the barium salt, hydrolyzed and the inosite separated in the usual manner. It melted at 215–16° (uncorr.) and gave the reaction of Scherrer.

The silver salt is amorphous and may consist of a mixture of silver salts of the acid in question, and for this reason variation in analyses of different fractions may be expected. Since the strychnine salt from which the silver salt was made has been shown to be pure all of the carbon and phosphorus in the silver salt must be attributed to the acid. The composition of the acid then can be calculated from analyses of the silver salt regardless of the fact that the silver salt may be a mixture of silver salts of the same acid. The error of analysis would of course be multiplied.

The silver salt agrees in composition to nonasilver inosite pentaphosphate and equally as well to a silver salt of the acid of the formula previously proposed by the writer. The percentage of carbon in the free acid as calculated from these analyses agrees with that calculated for inosite pentaphosphoric acid, and the phosphorus agrees likewise, but not so closely.

[1] *Loc. cit.*

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On account of the fact that the large amount of material obtained in the above work on wheat bran added considerably to the time required for purification and fractionation, and that a considerable amount of strychnine orthophosphate was obtained, probably as a product of hydrolysis, the work was repeated using smaller amounts of wheat bran.

1.5 kg. of wheat bran were digested for three hours with 16 liters of 0.2% hydrochloric acid and the process of separation and purification conducted as before. 32 g. of the crude syrupy acid were obtained and from this 35 g. of the purified strychnine salt melting at 220–2°. Analysis was conducted as already described. The results follow:

Calc. for tetrastrychnine inosite pentaphosphate: C, 56.33; H, 5.48; N, 5.84; P, 8.09; 7 H_2O, 6.57.

Found, Fraction 1: C, 55.87; H, 5.78; N, 5.48; P, 8.84; H_2O, 6.45.

Found, Fraction 2: C, 55.87; H, 5.70; N, 5.44; P, 8.62; H_2O, 6.25.

The salt corresponds in composition to that previously prepared.

The silver salt was prepared and analyzed as before. The results follow:

Calc. for nonasilver inosite pentaphosphate: C, 4.67; H, 0.52; P, 10.05; Ag, 62.96.

Found, Fraction 1: C, 4.49; H, 1.17; P, 10.68; Ag, 61.67.

Found, Fraction 2: C, 4.88; P, 10.04; Ag, 62.47.

Calc. for inosite pentaphosphoric acid: C, 12.41; H, 26.72.

Composition of free acid as calc. from mean analyses of Ag salt: C, 12.21; P, 26.80.

The results are in accord with those discussed above.

The strength of the acid (1.0%) used in extracting the material from wheat bran by the process of Anderson is greater than that employed in the above work. This might cause a decrease in the enzyme action and affect the composition of the product obtained. While the influence of enzymes has been found to be small under the conditions of the method used by the present writer, it was nevertheless considered desirable to analyze the material prepared with the use of the stronger acid.

1.5 kg. of wheat bran were digested for 3 hours with 16 liters of 1.0% hydrochloric acid and the process of separation and purification conducted as already described. 34 g. of the crude syrupy acid were obtained, and from this 34 g. of the purified strychnine salt melting at 220–2°. Analysis was conducted as before.

Calc. for tetrastrychnine inosite pentaphosphate: C, 56.33; H, 5.48; N, 5.84; P, 8.09; 7 H_2O, 6.57.

Found: C, 56.18; H, 5.73; N, 5.49; P, 8.81; H_2O, 6.50.

The silver salt was prepared and analyzed as before.

Calc. for octasilver inosite pentaphosphate: C, 5.02; H, 0.63; P, 10.80; Ag, 60.13.

Found: C, 4.90; H, 1.11; P, 10.47; Ag, 60.31.

Calc. for inosite pentaphosphoric acid: C, 12.41; P, 26.72.

Composition of free acid calc. from analyses of silver salt: C, 12.17; P, 26.02.

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The substances correspond in composition to those prepared with the 0.2% hydrochloric acid.

Separation of the Inosite Phosphoric Acid by the Method of Anderson.—The method by means of which Anderson[1] separated a product from wheat bran which he believed to be a salt of inosite hexaphosphoric acid, $C_6H_6(H_2PO_4)_6$, differs from that employed by the present writer. It is therefore of interest to determine whether this process gives the same results on the sample under examination as that of the present writer. The procedure was carried out as closely as possible as directed by Anderson. The barium salt thus prepared was analyzed after drying to constant weight at 105° in a vacuum over phosphorus pentoxide. Carbon was determined by mixing the sample with a fused and powdered mixture of lead chromate and potassium dichromate and burning in a current of oxygen. The results follow:

Found: C, 7.62; H, 1.96; P, 16.84; Ba, 37.56.
Composition of free acid as calc. from above analyses: C, 11.53; P, 26.73.

Calc. for inosite pentaphosphoric acid: C, 12.41; P, 26.72.
Calc. for inosite hexaphosphoric acid: C, 10.90; P, 28.18.

The phosphorus content corresponds to that of inosite pentaphosphoric acid, and the carbon content lies between that of inosite pentaphosphoric acid and that of inosite hexaphosphoric acid.

Since the barium salt is burned with great difficulty, the silver salt of the acid was prepared from the barium salt by decomposing the latter with sulfuric acid, precipitating the free acid with copper acetate, decomposing the copper salt with hydrogen sulfide, and preparing the silver salt from the ammonium salt as already described. Analysis was made as before. The results follow:

Calc. for octasilver inosite pentaphosphate: C, 5.02; H, 0.63; P, 10.80; Ag, 60.13.
Found: C, 5.03; H, 1.39; P, 10.66; Ag, 60.00.

Calc. for inosite pentaphosphoric acid: C, 12.41; P, 26.72.
Composition free acid calc. from analyses of silver salt: C, 12.37; P, 26.28.

The composition of the silver salt corresponds to that of a salt of inosite pentaphosphoric acid. It does not correspond to that of a salt of inosite hexaphosphoric acid. The composition of the free acid as calculated from analyses of the silver salt corresponds in carbon and phosphorus quite closely to that of inosite pentaphosphoric acid.

On the basis of the analyses reported on the preceding pages, the writer concludes that the inosite phosphoric acid separated from the sample of wheat bran by the several methods corresponds in composition to an inosite phosphoric acid of the formula $C_6H_6(OH)(H_2PO_4)_5$ inosite pentaphosphoric acid. The silver and strychnine salts correspond equally as well in composition to salts of the acid of the formula $C_{12}H_{41}O_{42}P_9$, the formula pre-

[1] N. Y. (Geneva) Expt. Sta., *Tech. Bull.* 40.

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viously proposed by the writer for the acid in wheat bran, but for theoretical reasons the first formula is to be preferred.

While this work confirms earlier work of the writer on the subject it is not claimed that the wheat bran examined does not contain other inosite phosphoric acids. The amounts of other acids present in the acid extract must, however, be small. Further evidence to this effect will be given further on.

The Occurrence of Inosite Pentaphosphoric Acid in Corn.—The crude acid was prepared as already described. From 10 kg. of corn meal and 40 liters of 0.2% hydrochloric acid 23 g. of the crude syrupy acid were obtained. Twenty-eight grams of the strychnine salt melting at 220–2° were obtained. This product was similar in crystal form and melting point to those previously prepared.

The melting point of the product remained unchanged on recrystallization and fractionation. The fractions were free from bases other than strychnine and from orthophosphoric acid. Analysis was made as described above. The results follow:

Calc. for tetrastrychnine inosite pentaphosphate: C, 56.33; H, 5.48; N, 5.84; P, 8.09.

Found, Fraction 1: C, 56.37; H, 5.35; N, 5.32; P, 8.63.

Found, Fraction 2: C, 55.95; H, 6.16; N, 5.30; P, 8.74.

The salt corresponds in composition to that calculated for tetrastrychnine inosite pentaphosphate.

The silver salt was prepared and analyzed as before:

Calc. for nonasilver inosite pentaphosphate: C, 4.67; H, 0.52; P, 10.05; Ag, 62.96.

Found, Fraction 1: C, 4.91; H, 0.94; P, 10.26; Ag, 62.15.

Found, Fraction 2: C, 4.95; H, 0.90; P, 10.04; Ag, 62.02.

Calc. for inosite pentaphosphoric acid: C, 12.41; P, 26.72.

Calc. for free acid, Fraction 1: C, 12.77; P, 25.69.

Calc. for free acid, Fraction 2: C, 12.83; P, 26.04.

The free acid was prepared from the strychnine salt, hydrolyzed, and the inosite separated in the usual way. It melted at 215–6° (uncorr.), and gave the reaction of Scherer.

The sample of corn examined contained an inosite phosphoric acid similar in composition to that obtained from wheat bran and cottonseed meal by the writer. The melting point of the strychnine salt is the same and it probably is the same acid.

This conclusion is not in accord with the view of Hart and Tottingham and the view of Anderson concerning the composition of the inosite phosphoric acid of corn. It is possible that samples from different localities might yield acids of different composition, and small amounts of other inosite phosphoric acids may be present.

The Occurrence of Inosite Pentaphosphoric Acid in Kafir Corn.—The separation of the crude acid and the preparation of the purified strych-

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nine salt was conducted as described above. The fraction of the salt melting at 220–2° was obtained as for cottonseed meal, wheat bran, and corn. It constituted about 75% of the product. It was purified by recrystallization from water and fractionated as before. The melting point remained unchanged at 220–2°. The fractions melting at this temperature were free from bases other than strychnine and from orthophosphoric acid. Analysis was made as before. The results follow:

Calc. for tetrastrychnine inosite pentaphosphate: C, 56.33; H, 5.48; N, 5.84; P, 8.09.

Found, Fraction 1: C, 55.96; H, 6.09; N, 5.56; P, 8.49.

Found, Fraction 2: C, 55.54; H, 5.87; N, 5.44; P, 8.59.

The silver salt was prepared and analyzed as before:

Calc. for nonasilver inosite pentaphosphate: C, 4.67; H, 0.52; P, 10.05; Ag, 62.96.

Found, Fraction 1: C, 5.04; H, 1.02; P, 10.42; Ag, 61.93.

Found, Fraction 2: C, 4.72; H, 0.72; P, 10.48; Ag, 62.06.

Calc. for inosite pentaphosphoric acid: C, 12.41; P, 26.72.

Composition of free acid calc. from analyses of silver salt:

Fraction 1: C, 13.04; P, 26.98.

Fraction 2: C, 12.26; P, 27.19.

The free acid was prepared from the strychnine salt by means of the barium salt, hydrolyzed and the inosite separated in the usual way. The inosite melted at 215–16° (uncorr.), and gave the reaction of Scherer. Combustion gave the following results:

Calc. for inosite, $C_6H_{12}O_6$: C, 40.00; H, 6.67. Found: C, 39.74; H, 6.30.

The composition of the strychnine salt, the silver salt, and of the free acid calculated from the composition of the silver salt agree with the formulas of inosite pentaphosphoric acid and its salts.

The principal organic phosphoric acid in kafir corn is an inosite phosphoric acid corresponding in composition to inosite pentaphosphoric acid, $C_6H_6(OH)(H_2PO_4)_5$.

The Occurrence of Inosite Pentaphosphoric Acid in Oats.—The separation of the crude acid and the preparation of the purified strychnine salt was conducted as before. Ten grams of the crude acid were obtained from 10 kg. of ground oats and 40 liters of 0.2% hydrochloric acid. The physical condition of the material made complete extraction of the acid difficult. A fraction of the strychnine salt melting at 220–2° (uncorr.) was obtained as with the plant products previously examined. It was purified by recrystallization without change in melting point. The amount of the purified material was too small for satisfactory fractionation. The product was nearly free from inorganic bases and from orthophosphoric acid. Analysis was conducted as before.

Calc. for tetrastrychnine inosite pentaphosphate: C, 56.33; H, 5.48; N, 5.84; P, 8.09; 8 H_2O, 7.51.

Found: C, 56.18; H, 5.98; N, 5.64; P, 7.45; H_2O, 7.45.

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The silver salt was prepared and analyzed as before:

Calc. for nonasilver inosite pentaphosphate: C, 4.67; H, 0.52; P, 10.05; Ag, 62.96.
Found: C, 4.84; H, 1.02; P, 10.21; Ag, 61.56.
Calc. for inosite pentaphosphoric acid: C, 12.41; P, 26.72.
Composition of free acid calc. from silver salt: C, 12.41; P, 26.15.

The ammonium salt of the acid was prepared from the strychnine salt and hydrolyzed in a sealed tube with sulfuric acid in the usual manner. Inosite was separated as usual and recrystallized from alcohol and ether. The product had the characteristic appearance of inosite, melted at 216–18° (uncorr.) and gave the reaction of Scherer. Since the principal organic phosphoric acid of oats has already been shown to be an inosite phosphoric acid[1] further evidence as to the identity of the inosite was considered unnecessary.

The composition of the strychnine salt, of the silver salt, and of the free acid as calculated from analysis of silver salt, agree with the formula of inosite pentaphosphoric acid and its salts, and the writer therefore concludes that the principal inosite phosphoric acid in the sample of oats examined corresponds in composition to inosite pentaphosphoric acid, $C_6H_6(OH)(H_2PO_4)_5$, and not to that of the so-called phytic acid, $C_2H_8P_2O_9$, as obtained by Hart and Tottingham, nor to that of inosite hexaphosphoric acid, $C_6H_6(H_2PO_4)_6$, as obtained by Anderson, from oats.

The Occurrence of Inosite Pentaphosphoric Acid in Wheat Shorts.—The crude acid was separated in the manner already described and the strychnine salt prepared and purified as before. 16 g. of the crude acid were obtained from 1.5 kg. of material. The fraction of the strychnine salt melting at 220–2° (uncorr.) was obtained as before. As usual it constituted the principal fraction of the crude salts. The melting point remained unchanged on recrystallization. The material was free from bases other than strychnine and from orthophosphoric acid. Analysis was conducted as before:

Calc. for tetrastrychnine inosite pentaphosphate: C, 56.33; H, 5.48; N, 5.84; P, 8.09; 7 H_2O, 6.57.
Found, Fraction 1: C, 56.00; H, 5.66; N, 5.64; P, 8.27; H_2O, 7.00.
Found, Fraction 2: C, 56.01; H, 5.83; N, 5.48; P, 8.78; H_2O, 6.00.

The silver salt was prepared and analyzed as before:

Calc. for nonasilver inosite pentaphosphate: C, 4.67; H, 0.52; P, 10.05; Ag, 62.96.
Found, Fraction 1: C, 4.73; H, 1.06; P, 10.22; Ag, 61.76.
Calc. for inosite pentaphosphoric acid: C, 12.41; P, 26.72.
Composition of free acid calc. from silver salt: C, 12.19; P, 26.34.

The ammonium salt of the acid was hydrolyzed in the usual manner and inosite separated and recrystallized. It melted at 216–218° (uncorr.) and gave the reaction of Scherer. Analysis gave the following results:

[1] Hart and Tottingham, Wis. Expt. Sta., *Res. Bull.* 9; Anderson, *J. Biol. Chem.*, 17, 151.

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Calc. for inosite, $C_6H_{12}O_6$: C, 40.00; H, 6.67. Found: C, 40.36; H, 6.49.

The composition of the strychnine salt, of the silver salt, and of the free acid as calculated from analysis of silver salt agree with the formula of inosite pentaphosphoric acid and its salts.

The principal organic phosphoric acid in the sample of wheat shorts examined is an inosite phosphoric acid corresponding in composition to inosite pentaphosphoric acid, $C_6H_6(OH)(H_2PO_4)_5$.

The Occurrence of Inosite Pentaphosphoric Acid in Rice Bran.—The acid was separated and the strychnine salt prepared and fractionated as already described. A fraction melting at 220–2° (uncorr.) was obtained as before. 36 g. of the crude acid were obtained from 1250 g. of rice bran. The purified strychnine salt melting at 220–2° constituted about 75% of the crude salts. The product was free from bases other than strychnine and from orthophosphoric acid. It was dried and analyzed in the usual manner.

Calc. for tetrastrychnine inosite pentaphosphate: C, 56.33; H, 5.48; N, 5.84; P, 8.09; 7 H_2O, 6.57.

Found, Fraction 1: C, 55.67; H, 5.75; N, 5.33; P, 8.64; H_2O, 6.26.

Found, Fraction 2: C, 55.93; H, 6.01; N, 5.69; P, 8.81; H_2O, 6.40.

The silver salt was prepared and analyzed with the following results:

Calc. for nonasilver inosite pentaphosphate: C, 4.67; H, 0.52; P, 10.05; Ag, 62.96.

Found, Fraction 1: C, 4.78; H, 0.63; P, 10.24; Ag, 62.19.

Calc. for inosite pentaphosphoric acid: C, 12.41; P, 26.72.

Composition free acid calc. from silver salt: C, 12.45; P, 26.67.

Inosite was separated from the ammonium salt by hydrolysis and purification in the usual manner. It melted at 216–18° (uncorr.), gave the reaction of Scherer and had the crystal form and sweetish taste of inosite. Since the principal organic phosphoric acid of rice bran has already been shown to be an inosite phosphoric acid[1] analysis of the inosite was considered unnecessary.

The composition of the strychnine salt, of the silver salt, and of the free acid as calculated from analysis of silver salt, agree with the formula of inosite pentaphosphoric acid and its salts. These results differ from those obtained by Alice R. Thompson[2] who used Anderson's method of separation. The carbon content of the acid as calculated from her results by the writer would be 10.54 as against 12.45 reported here and the phosphorus content 25.58 as against 26.67 found by the writer.

The writer concludes that the principal inosite phosphoric acid in the sample of rice bran examined corresponds in composition to inosite pentaphosphoric acid, $C_6H_6(OH)(H_2PO_4)_5$.

[1] Alice R. Thompson, *J. Agr. Res.*, 3, 425 (1915); Suzuki, *et al.*, *Bull. Coll. Agr. Tokyo*, 7, 495–502, 503–512.

[2] *Loc. cit.*

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The Occurrence of Inosite Pentaphosphoric Acid in Rice Polish.—Alice R. Thompson[1] has shown that unpolished rice contains an inosite phosphoric acid and that polished rice contains practically none of this compound. The presence of inosite phosphoric acid in rice polish is therefore rendered certain.

The acid was separated and the strychnine salt prepared and fractionated as already described. 44 g. of the free acid were obtained from 1250 g. of the rice polish, and the strychnine salt melting at 220–2° which was obtained as before constituted about 75% of the crude salts. The substance was free from bases other than strychnine and from orthophosphoric acid. It was dried and analyzed as before:

Calc. for tetrastrychnine inosite pentaphosphate: C, 56.33; H, 5.48; N, 5.84; P, 8.09; 7 H_2O, 6.57.
Found, Fraction 1: C, 56.29; H, 6.01; N, 5.52; P, 8.54; H_2O, 6.50.
Found, Fraction 2: C, 55.56; H, 6.09; N, 5.44; P, 8.78; H_2O, 5.83.

The silver salt was prepared and analyzed as before:

Calc. for nonasilver inosite pentaphosphate: C, 4.67; H, 0.52; P, 10.05; Ag, 62.96.
Found, Fraction 1: C, 4.86; H, 1.01; P, 10.30; Ag, 61.88.
Calc. for inosite pentaphosphoric acid: C, 12.41; P, 26.72.
Composition free acid calc. from silver salt: C, 12.55; P, 26.62.

The ammonium salt of the acid, prepared from the strychnine salt, was hydrolyzed and the inosite separated and purified in the usual way. It melted at 216–18° (uncorr.) and gave the reaction of Scherer. Analysis gave the following results:

Calc. for inosite, $C_6H_{12}O$: C, 40.00; H, 6.67. Found: C, 40.11; H, 6.47.

The composition of the strychnine salt, of the silver salt, and of the free acid as calculated from analyses of the silver salt, agree with the formula of inosite phosphoric acid and its salts. The writer concludes, therefore, that the principal inosite phosphoric acid in the sample of rice polish examined corresponds in composition to inosite pentaphosphoric acid, $C_6H_6(OH)(H_2PO_4)_5$.

Concerning the Presence of Phosphorus Compounds other than Inosite Pentaphosphoric Acid in the Samples.—While the crystalline product described above constituted the principal fraction of the several products, the fact that there was in every case an uncrystallizable residue rendered a quantitative knowledge of the amount of inosite pentaphosphoric acid desirable. A method has been devised[2] which determines the compound the writer believes to be inosite pentaphosphoric acid without being affected by other compounds in the plant extract. Results on the samples of materials under examination are given below:

[1] *Loc. cit.*
[2] Rather, THIS JOURNAL, 39, 2506 (1917).

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Material.	Phosphorus in % of total acid-soluble phosphorus. (A).	(B).	(C).
Corn	75	18	7
Cottonseed meal	95	9	0
Wheat shorts	84	8	8
Kafir corn	74	13	13
Wheat bran	89	3	8
Rice bran	87	19	0
Rice polish	93	10	0
Oats	81	8	11

(A) Phosphorus in the form of inosite pentaphosphoric acid.
(B) Inorganic phosphorus (Forbes method).
(C) Phosphorus in other forms, by difference.

From 75 to 95% of the acid-soluble phosphorus is shown by the above figures to consist of the compound which has been found to correspond in composition to inosite pentaphosphoric acid. Of the amount remaining, from 3 to 18% consists of inorganic phosphorus, leaving from 0 to 13% to be accounted for in other forms of phosphorus. Repeated attempts have been made to obtain a definite compound from the noncrystalline material obtained in the preparation of the purified strychnine salt of the inosite pentaphosphoric acid. In a few cases small amounts of a substance corresponding in composition to strychnine orthophosphate and melting at the temperature of distrychnine orthophosphate were obtained. Analysis of silver salts prepared from these indicated that there was practically no carbon in the free acid and the silver salts had the characteristic canary yellow color of silver orthophosphate. In another case small amounts of a crystalline strychnine salt free from phosphorus were obtained.

The method of preparation of the crude inosite phosphoric acid was designed to include all of the phosphorus compounds soluble in the extracting medium, the separation and purification being made by means of the strychnine salt. It is evident that the noncrystalline material separated from the strychnine inosite pentaphosphate would consist of a mixture of all of those acids, whether phosphorus containing or not, which were extracted by the solvent and whose copper salts are difficultly soluble in water. On account of the very large bulk of the copper precipitate, quantitative removal of soluble matter is impracticable, the copper salts, even when compressed by suction on a Buchner funnel, frequently having a bulk of 500 cc. The mother liquors from the strychnine fractionation would then be expected to contain small amounts of hydrochloric acid and acetic acid (both introduced in the process), all of the orthophosphoric acid, and various unknown plant acids, all in the form of strychnine salts. This does not interfere with the separation and purification of the principal compound in the mixture, but it renders the identification of any constituent present

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in very small amount quite difficult. For that reason the writer is not prepared to state that inosite monophosphate, inosite triphosphate, or other inosite phosphoric acids are not present in the samples in small amounts, but it is evident that the figures given above that they cannot be present in amounts much exceeding ten percent of the total acid-soluble phosphorus.

Acknowledgment.—The writer is indebted to Mr. R. H. Ridgell for the preparation of some of the crude acids and for making some nitrogen and phosphorus determinations.

Summary.

1. An inosite phosphoric acid has been separated from wheat bran by means of its crystalline strychnine salt and its composition ascertained by analysis of strychnine and silver salts. An acid corresponding in composition to the formula $C_{12}H_{41}O_{42}P_9$ is indicated by these results, which formula is the one previously proposed by the writer for this material. The formula $C_6H_6(OH)(H_2PO_4)_5$, inosite pentaphosphoric acid, agrees equally as well with the results, and since it is numerically almost one-half of the first formula and is that of a theoretically possible compound, it is adopted as the more desirable.

2. Increasing the strength of the extracting medium from 0.2% to 1.0% hydrochloric acid in order to inhibit all enzyme action on the compound gave results in accord with the above.

3. The use of the method of preparation on the basis of which it has been stated that inosite hexaphosphoric acid was separated from wheat bran gave results concordant with the above.

4. The principal inosite phosphoric acid of samples of corn, rice bran and oats was found to correspond in composition to inosite pentaphosphoric acid, and neither to inosite hexaphosphoric acid nor to phytic acid, $C_2H_8P_2O_9$.

5. The principal phosphoric acid of samples of kafir corn, wheat shorts, and rice polish, was found to be organic and to be an inosite phosphoric acid corresponding in composition to inosite pentaphosphoric acid.

6. The possibility of the presence of other inosite phosphoric acids in the samples examined is not excluded by this work, but it is shown that the compound corresponding in composition to inosite pentaphosphoric acid together with the orthophosphoric acid constitute on, and average 95% of the acid-soluble phosphorus.

FAYETTEVILLE, ARK.

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[CONTRIBUTION FROM THE LABORATORIES OF ORGANIC CHEMISTRY, UNIVERSITY OF ILLINOIS.]

THE SCALE OF INFLUENCE OF SUBSTITUENTS IN PARAFFINE MONOBASIC ACIDS AND THE CORRELATION OF IONIZATION WITH STRUCTURE.

III. THE DIVALENT OXYGEN ATOM IN THE ε-POSITION.[1]

BY C. G. DERICK AND R. W. HESS.

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CONTENTS.—I. Historical Part. II. A Comparison of the Ostwald and Derick Factors. III. The Ionization Constants of Certain Organic Acids Recalculated Using Modern Conductance Units. IV. The Theoretical Basis for the Measurement of the Influence of a Substituent upon the Reaction Ionization, the *Place Influence*. V. The Relative ε-Place Influence of an Atom of Oxygen, Substituted into Monobasic Paraffine Acids, upon the Reaction Ionization. VI. Synthesis of δ-Acetovalerianic Acid and Its Intermediate Compounds, and a Study of the Factors Which Control the Yields at Each Step of the Process. 1. Trimethylene Glycol. 2. Trimethylene Bromide. 3. γ-Bromobutyronitrile. 4. δ-Cyano-α-acetovalerianic Ethyl Ester. 5. 1,7-Dicyano-4-aceto-4-carboxethyl Heptane. 6. δ-Acetovalerianic Acid and Its Sodium Salt. VII. Electrical Conductivity Measurements. 1. Method and Apparatus. 2. Preparation of Solutions and Procedure of Measurements. 3. Symbols Used for the Conductivity Data. 4. Conductance and Ionization Constant of δ-Acetovalerianic Acid. 5. Conductance Measurements on the Sodium Salt of δ-Acetovalerianic Acid. 6. The Application of "Calculated" Λ_0 to the Conductance Data of δ-Acetovalerianic Acid. VIII. The Ionization Constant of, and the Application of "Calculated" Λ_0 to the Conductance Data of, Normal Heptanoic Acid. IX. Summary.

I. Historical Part.

This investigation is the continuation of the work of one of us upon the study of the effect of the nature and the position of one atom upon the tendency of another atom within the same molecule to enter into chemical reaction. The reaction chosen was the ionization of organic acids because of the comparative simplicity of the theoretical and laboratory treatment of this process. Incidentally, this also affords a means of correlating ionization with the structure of organic acids. On the synthetic side, a study of the factors which control the yields at each step of the process was made.

Van't Hoff[2] was the first to point out that in general the ionization constant of an acid depends on the nature, number and position of the substituents. He observed that the influence of a substituent usually decreased with an increasing number of atoms intervening between it and the acidic hydrogen. Exceptions which are difficult to explain have been found. Irregularities have been observed especially in the unsat-

[1] The experimental part of this paper was presented at the Urbana meeting of the American Chemical Society, 1916. From a thesis, submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Illinois.

[2] "Lectures on Theoretical and Physical Chemistry," Part III, pp. 113–143.

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urated aliphatic and in aromatic acids and in acids substituted with certain groups as the anilino group C_6H_5NH—. Furthermore, there are radicals of feeble polarity which increase the degree of ionization when substituted into some acids and decrease it when substituted into others. Many attempted explanations have been offered but they lack the desired generality. These will not be discussed here, since consideration is to be given primarily to the measurement of these forces rather than to their causes. Michael[1] has stated that "If we number a certain atom in any normal carbon chain by the figure 1, our present knowledge of the combined mutual influence between this atom and others in the molecule is expressed by the following scale of combined influence, the number indicating the degree of removal and the extent of the influence decreasing in the order given, 2–3–5–6–4–7–(9–10–11)–8." More recently, Derick[2] contended that for strongly negative atoms and radicals, substituted into monobasic paraffine acids, the order should be 1–2–3–4–5–6–7–8–9–10–11,[3] for the reaction of ionization.

In the complete study of this problem it must first be decided if a single scale of influence is applicable to all chemical reactions. This does not seem probable in the light of the above discussion and no decision can be made until accurate quantitative data are available for each reaction in question. A review of Michael's scale of influence shows that positions 4 and 8 are anomalous. Unfortunately no acids with a negative atom in position 4 can be prepared in a pure state and accurately measured, since such acids as Cl.COOH, Br.COOH, etc., are unknown. However, it is possible to measure the influence of a negative atom in position 8(δ) for the reaction ionization. A further study of the literature shows that no measurements of the ionization of acids with the negative atom in positions beyond the (δ) are known. Hence in order to test the relative magnitude of 8 and 9 in Michael's scale, acids with negative atoms in these positions must be prepared and measured. The experimental part of this investigation deals with the preparation and measurement of the ionization constant of ϵ-oxoheptanoic acid (δ-acetovalerianic acid), in which the oxygen atom is in Michael's position 9(ϵ).

Before accurate conclusions can be formed it is necessary to determine the true method of measuring the influence of one atom upon another for the reaction under consideration. It will be shown in a later section that the ionization constant is not an exact measure of this influence for the reaction ionization, although it may serve for estimating the relative order of a scale of influence in many cases.

[1] *J. prakt. Chem.*, **168**, 231 (1899); *Ber.*, **39**, 2139 (1906); THIS JOURNAL, **32**, 999 (1910).

[2] *Ibid.*, **33**, 1182 (1911).

[3] NOTE.—This is using Michael's nomenclature numbering the carboxylic hydrogen atom 1, contrary to the accepted Geneva method for organic acids.

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Ostwald[1] was the pioneer in the other phase of the problem. The ionization constant of the substituted acid divided by that for the unsubstituted acid, he called the factor for the substituent in a given position. Bethman,[2] Holleman,[3] and Wegscheider[4] continued the study, using this factor. By its use it was found possible to calculate approximately the ionization constants of several poly-substituted acids, especially in the aromatic series.

In 1911 Derick[5] proposed the use of the expression $\frac{\log k_o}{\log k_n} - 1$, where k_n is the ionization constant of the substituted acid and k_o the constant for the corresponding unsubstituted acid, as a more general and useful expression. Many calculations were made definitely, establishing his claim.

II. A Comparison of the Ostwald and Derick Factors.

In 1912 Wegscheider[6] compared the use of the Ostwald factor with Derick's place factor in considerable detail, but with some misleading conclusions. He stated:

"Ein Nachteil des Derickschen Ansatzes ist jedenfalls, dass er rechnerisch viel unbequemer ist als der Ostwaldsche. Er könnte daher nur dann mit dem Ostwaldschen erfolgreich in Wettbewerb treten, wenn er sonstige Vorzüge hätte. Als solche könnten in Betracht kommen: 1, Eine bessere theoretische Begründung; 2, das Auftreten einfacherer Zahl einbeziehungen zwischen den Factoren; 3, die genuarere Darstellung der Dissoziationkonstanten in jeden Fällen, wo sich die beiden Ansätze unterscheiden."

In the first place it is evident that merely for the purpose of correlation the question of a theoretical basis does not necessarily enter. Any formula which expresses the relationships most accurately and generally in a convenient form will be best. After discussing his first point rather vaguely, Wegscheider says:

"Dem gegenüber gibt das Ostwaldsche Factorengesetz, wie aus Gleichung (4)[7] ersichtlich ist, eine einfache und durchsightige Beziehung zwischen Konstitution und RT ln k'."

Wegschieder's use of the logarithm of the Ostwald factor concedes the very point of Derick's contention, namely, that the logarithm of the ionization constant is a more fundamental function for this purpose. The reason for this will be seen in the following discussion. It should be kept in mind, however, that the logarithmic function of the ionization constant had not been used in this connection, previous to its use by

[1] *Z. phys. Chem.*, **3**, 170, 369–422 (1889).
[2] *Ibid.*, **5**, 385–422 (1890).
[3] *Rec. des Tran. Chim.*, **20**, 360–364 (1901).
[4] *Monatsh.*, **16**, 153–158 (1895); **23**, 287–316 (1902); **26**, 1265 (1905).
[5] THIS JOURNAL, **33**, 1152–1189 (1911); **34**, 74–82 (1912).
[6] *Z. Elektrochem.*, **18**, 277–281 (1912).
[7] $\log k' = \log k \log a \log b$.....

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Derick. Wegscheider suggested its use here, but in another form, only, after its value had been recognized by Derick.

In discussing the second and third points raised by Wegscheider, the two uses of a correlation of ionization and structure should be kept clearly in mind. The first use is the calculation of the ionization constant from the structure, Wegscheider's third point, which will be discussed presently. The second use is the determination of the position of a substituent in an acid from a knowledge of its ionization constant. In this connection Derick[1] has previously shown that the place factors for the α, β, γ and δ positions for a strongly negative substituent stand roughly in the ratio of 1, 1/3, 1/9, 1/27, respectively. This regularity he called the *rule of thirds*. From this it is evident that it is possible to determine the position of the substituent in a negatively substituted monobasic paraffine acid from its ionization constant. This involves Wegscheider's second point. In discussing this he has made an unfortunate use of Derick's place factor. He claimed that if the rule of thirds holds, the factor for a given position divided by that for the next succeeding one should give 3 in each case. This is misleading at first thought, since it is evident that it is only necessary for the result to be nearer to 3 than to 9 or to 1, in order to determine the position of the substituent. Only in one case given would there be any question as to the position of the substituent. This was obtained by dividing the γ-place factor by the δ-place factor for iodine.

The rule of thirds is the most striking advantage of the Derick place factors α, β, γ and δ over the corresponding Ostwald factors a, b, c and d. No such regular and simple relationship between the Ostwald factors is obvious. The numerical values of both the Ostwald and Derick factors are given in Table I. The relationships are best seen in Table II, in which the α-place factor is taken as unity in each case and the place factors for the same substituent in the succeeding positions are expressed in fractions of the α-factor. The Ostwald factors are treated in a similar manner.

While it is true that it can be shown, as Wegscheider has done, that the Ostwald factors a, b, c and d should obey an approximate rule of cube roots, it should be observed that it had not been noted until Derick stated his rule of thirds. In reality, Wegscheider expressed the Ostwald factors in terms of Derick's factors and found the cube root rule. Practically, a cube root rule would be much more difficult to use in making calculations.

This phase of the correlation of ionization and structure, namely, the determination of structure, shows unquestionably that Derick has advanced this problem by the use of the logarithm of the ionization constant.

[1] THIS JOURNAL, 33, 1181–1185 (1911).

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TABLE I.—NUMERICAL VALUES OF FACTORS.

Substituent. Acid substituted.	Ostwald factor. $\frac{k_H}{k_o}$.				Derick's place factor $\frac{\log k_o}{\log k_H} - 1$.				Place influence $\frac{RT}{\log k_H - \log k_o}$.			
	a.	b.	c.	d.	α.	β.	γ.	δ.	$\frac{I_{\alpha S} - I_{\alpha H}}{RT}$.	$\frac{I_{\beta S} - I_{\beta H}}{RT}$.	$\frac{I_{\gamma S} - I_{\gamma H}}{RT}$.	$\frac{I_{\delta S} - I_{\delta H}}{RT}$.
Chlorine												
Acetic	79	..	..	..	0.67	..	..	..	1.90	..	..	..
Propionic	110	6.5	..	..	0.72	0.195	..	..	2.04	0.81	..	..
Butyric	94	5.9	1.98	..	0.69	0.191	0.065	..	1.97	0.77	0.298	..
Valerianic	..	..	..	1.26	..	..	..	0.0224	..	..	..	0.100
Average	94	6.2	1.98	1.26	0.69	0.193	0.065	0.0224	1.97	0.79	0.298	0.100
Bromine												
Acetic	71	..	..	..	0.64	..	..	..	1.85	..	..	..
Propionic	80	7.0	..	..	0.64	0.212	..	..	1.91	0.85	..	..
Butyric	67	..	1.75	..	0.62	..	0.0520	..	1.84	..	0.243	..
Valerianic	..	..	..	1.18	..	..	..	0.0153	..	..	..	0.073
Average	72	7.0	1.75	1.18	0.63	0.212	0.0520	0.0153	1.86	0.85	0.243	0.073
Iodine												
Acetic	38	..	..	..	0.50	..	..	..	1.58	..	..	..
Propionic	..	6.5	..	..	..	0.199	..	..	..	0.81	..	..
Butyric	..	..	1.52	..	..	..	0.0392	..	..	..	0.182	..
Valerianic	..	..	..	1.05	..	..	..	0.0050	..	..	..	0.0239
Average	38	6.5	1.52	1.05	0.50	0.199	0.0392	0.0050	1.58	0.81	0.182	0.0239
Hydroxyl												
Acetic	8.1	..	..	..	0.238	..	..	..	0.91	..	..	..
Propionic	10.3	2.33	..	..	0.262	0.081	..	..	1.01	0.37	..	..
Butyric	..	..	1.27	..	..	..	0.0223	..	..	..	0.105	..
Isobutyric	7.4	..	..	..	0.218	..	..	..	0.87	..	..	..
Valerianic	..	..	1.25	..	..	..	0.0206	..	..	..	0.097	..
Average	8.6	2.33	1.26	..	0.242	0.081	0.0214	..	0.93	0.37	0.101	..

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TABLE II.—RATIOS TO THE ALPHA VALUES.

Substituent.	Ostwald factors. $\frac{a}{a}$.	$\frac{b}{a}$.	$\frac{c}{a}$.	$\frac{d}{a}$.	Derick place factors. $\frac{\alpha}{\alpha}$.	$\frac{\beta}{\alpha}$.	$\frac{\gamma}{\alpha}$.	$\frac{\delta}{\alpha}$.
Chlorine.....	1	0.066	0.0213	0.0134	1	0.279	0.094	0.0324
Bromine.....	1	0.097	0.0243	0.0164	1	0.336	0.082	0.0243
Iodine.....	1	0.171	0.0400	0.0278	1	0.398	0.078	0.0100
Hydroxyl.....	1	0.271	0.1460	..	1	0.334	0.088	..

	Place influences. $\frac{I_{\alpha s}-I_{\alpha H}}{I_{\alpha s}-I_{\alpha H}}$.	$\frac{I_{\beta s}-I_{\beta H}}{I_{\alpha s}-I_{\alpha H}}$.	$\frac{I_{\gamma s}-I_{\gamma H}}{I_{\alpha s}-I_{\alpha H}}$.	$\frac{I_{\delta s}-I_{\delta H}}{I_{\alpha s}-I_{\alpha H}}$.
Chlorine.....	1	0.401	0.151	0.0507
Bromine.....	1	0.455	0.131	0.0392
Iodine.....	1	0.513	0.115	0.0151
Hydroxyl.....	1	0.398	0.109	..

In connection with the third point Derick[1] has shown that, since the place factors for a given substituent follow the rule of third, it is necessary to know only the alpha factor for this substituent and the ionization constant of the corresponding unsubstituted acid in order to be able to calculate the ionization constant of an acid with this substituent in any position of a paraffine monobasic acid. He[2] has also shown that it is possible to calculate the ionization constants of several poly-substituted paraffine monobasic acids by the use of his rule of thirds.

In the aromatic series Derick[3] has found that no constant ratio exists between the ortho, meta and para place factors for substituents in the mono-substituted benzoic acids. He has shown, however, that with the aid of the place factors it is possible to calculate the approximate ionization constants of, as well as the structure of, many poly-substituted benzoic acids.

Obviously, the problem of correlating the ionization and structure of negatively substituted organic acids has been advanced by the use of the logarithm of the ionization constant.

III. The Ionization Constants of Certain Organic Acids Recalculated Using Modern Conductance Units.

The ionization data used in compiling the above tables are expressed in international ohms. The values for the equivalent conductances of the hydrogen and sodium ions at zero concentration (infinite dilution) are 34.7 and 51.5, respectively, at 25°. This has necessitated the recalculation of most of the data given by the original investigators.

[1] THIS JOURNAL, 33, 1185–1189 (1911).
[2] *Ibid.*, 33, 1187–1189 (1911).
[3] *Ibid.*, 34, 74–82 (1912).

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TABLE III.—IONIZATION CONSTANTS OF ORGANIC ACIDS.

Acid.	Ref.	$k \times 10^4$.
Acetic	1	0.185
Propionic	2	0.132
Butyric	2	0.149
Isobutyric	2	0.141
Valerianic	2	0.159
Chloroacetic	2	14.7
Bromoacetic	2	13.2
Iodoacetic	3	7.0
Hydroxyacetic	2	1.50
Phenylacetic	2	0.554
α-Chloropropionic	4	14.6
β-Chloropropionic	4	0.859
α-Bromopropionic	3	10.6
β-Bromopropionic	3	0.93
β-Iodopropionic	2	0.86
α-Hydroxypropionic	2	1.36
β-Hydroxypropionic	2	0.307
α-Phenylpropionic	2	0.422
β-Phenylpropionic	2	0.224
α-Chlorobutyric	4	14.0
β-Chlorobutyric	4	0.885
γ-Chlorobutyric	4	0.296
α-Bromobutyric	3	10.2
γ-Bromobutyric	4	0.261
γ-Iodobutyric	4	0.225
γ-Hydroxybutyric	5	0.190
α-Hydroxyisobutyric	2	1.05
δ-Chlorovalerianic	4	0.200
δ-Bromovalerianic	4	0.188
δ-Iodovalerianic	4	0.168
γ-Hydroxyvalerianic	5	0.199

IV. The Theoretical Basis for the Measurement of the Influence of a Substituent upon the Reaction Ionization, the *Place Influence*.

It follows from thermodynamics that if an acid passes from unit concentration of un-ionized molecules to unit concentration of its ions, the combined effect of all the atoms in the molecule upon the tendency of the reaction to occur is expressed by the equation

$$A = RT \ln k,$$

in which k is the ionization constant. If a substituent is introduced into this acid, the effect of all the atoms upon the reaction is readily seen to be

$$A - I_H + I_s = RT \ln k_1,$$

[1] J. Kendall, *J. Chem. Soc.*, **101**, 1283 (1912).
[2] W. Ostwald, *Z. phys. Chem.*, **3**, 170–199 (1889).
[3] P. Walden, *Ibid.*, **10**, 638–664 (1892).
[4] K. Drucker, *Ibid.*, **52**, 643 (1905).
[5] P. Henry, *Ibid.*, **10**, 120 (1892).

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where k_1 is the ionization constant of the substituted acid, I_H the influence of the replaced hydrogen atom and I_s the influence of the substituent upon the reaction. By combining the two equations we have

$$I_s - I_H = RT (\ln k_1 - \ln k).$$

In order to solve this equation for I_s it is evidently necessary to know the value of I_H or it must be proven to be negligibly small. At present there is not sufficient data obtainable for calculating the influence of the hydrogen atom. In this study $I_s - I_H$ has been called the *place influence* and $(I_s - I_H)/RT$ the *relative place influence* of a substituent under consideration. Obviously, it is necessary to know only the ionization constants of the substituted and corresponding unsubstituted acids, for a given substituent in different positions of an acid, in order to be able to calculate the relative place influences. That is, if we wish to compare the relative values of the place influences, RT is the same in each case and cancels out in the ratio, so we have, for example,

$$\frac{I_{\beta Cl} - I_{\beta H}}{I_{\alpha Cl} - I_{\alpha H}} = \frac{\log k_{\beta Cl} - \log k_o}{\log k_{\alpha Cl} - \log k_o}.$$

These relative values are given in Table I. The place influence for a given substituent is seen to have approximately the same value for the same position in each acid, and to follow, roughly, the rule of thirds for the α, β, γ and δ positions. This is best seen in Table II, where the α-place influence is taken as unity in each case.

V. The Relative ϵ-Place Influence of an Atom of Oxygen, Substituted into Monobasic Paraffine Acids, upon the Reaction Ionization.

As previously stated, the primary object of this investigation was to determine the relative ϵ-influence of an atom of oxygen upon the reaction ionization when substituted into paraffine monobasic acids. In the preceding section it was shown that the ionization constants of the substituted and the corresponding unsubstituted acids must be known in order to calculate this value. In the following sections the ionization constant of δ-acetovalerianic acid is shown to be 1.926×10^{-5}. From the considerations given in Section VIII, the value 1.4×10^{-5} was chosen as the approximate ionization constant of normal heptanoic acid. From these values the approximate relative oxygen ϵ-place influence, $I_{\epsilon O} - I_{\epsilon 2(H)}/RT$, for the reaction under consideration, is found to be 0.14.

Unfortunately, the uncertainty concerning the correct value for the ionization constant of heptanoic acid destroys the accuracy desired in the value for this place influence. This is seen most clearly when the criterion "calculated" Λ_o is applied to the measurements of heptanoic acid by Franke and Drucker. See Section VIII.

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VI. Synthesis of δ-Acetovalerianic Acid and Its Intermediate Compounds, and a Study of the Factors Which Control the Yields at Each Stop of the Process.

The following method has not been previously used for making δ-acetovalerianic acid. Trimethylene glycol was converted into trimethylene bromide and from the latter γ-bromobutyronitrile was prepared. This was condensed with acetoacetic ester to give δ-cyano-α-acetovalerianic ethyl ester which was hydrolyzed to δ-acetovalerianic acid. These reactions afford a striking support of the use of the factors controlling yields as applied by the senior author and his students.

1. Trimethylene Glycol.—The literature shows that this substance has usually been prepared from trimethylene bromide, and it has long been known that it can be obtained from glycerine by the action of bacteria. Certain by-products on the American market, such as "Blizzard, Anti-Freeze," consist mainly of this substance. "Blizzard" was used as the source of the trimethylene glycol in this investigation and was obtained pure in an 80–90% yield by fractional distillation.

2. Trimethylene Bromide.—Trimethylene bromide has previously been prepared by the action of hydrobromic acid upon allyl bromide and upon trimethylene glycol under various conditions, usually in a sealed tube. The disadvantages of these methods are obvious, especially for the preparation of large quantities of the substance.

Excellent yields of trimethylene bromide were obtained, in this work, from the action of aqueous hydrobromic acid on trimethylene glycol without the inconveniences of the sealed tube method. The following equilibria will be established:

$$HOCH_2.CH_2.CH_2OH + HBr \rightleftharpoons HOCH_2.CH_2.CH_2Br + H_2O$$

$$HOCH_2.CH_2.CH_2Br + HBr \rightleftharpoons BrCH_2.CH_2.CH_2Br + H_2O$$

From a consideration of these equilibria it is predicted that the greater the concentration of the hydrobromic acid the better should be the yield of trimethylene bromide. This is forcefully substantiated in the following two experiments:

The Norris Method.—The technique of the Norris method[1] for making halides from alcohols was first used. 235 g. of trimethylene glycol and 1060 cc. of constant boiling aqueous hydrobromic acid were refluxed together for six hours. These amounts are equivalent to one mole of glycol to three moles of hydrogen bromide. Since the glycol is not very volatile with steam the mixture was distilled in order to remove the water and the bromide first, causing the residue to become concentrated with the glycol and hydrobromic acid, thus displacing the equilibria to favor the yield of the trimethylene bromide. The latter practically all came over

[1] Norris, "Experimental Organic Chemistry," 1915, p. 100.

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with the first 700 cc. of distillate, forming a clear, oily, bottom layer. The last 350 cc. was practically pure 48% aqueous hydrobromic acid.

The oily layer was separated and distilled. Since it boiled over a considerable range of temperature it was proven to be impure. Consideration of the above equilibria predicts it to contain some γ-bromopropyl alcohol and trimethylene glycol. In order to remove these, the product was washed twice with 100 cc. of sulfuric acid (sp. gr. 1.84), twice with an equal volume of water, once with a dilute carbonate solution, and finally, once again with an equal volume of water. During the washing with sulfuric acid it was necessary to keep the mixture cool and to rotate cautiously in order to prevent emulsification. The product was dried over $CaCl_2$ and was found to distil constant at 165°. The yield was 330 g. or 53% of the theoretical.

Method II.—The second method gave much better results. The principle involved was to reflux one mole of trimethylene glycol with enough constant boiling aqueous hydrobromic acid to furnish three moles of hydrogen bromide, as before, and then two moles more of gaseous hydrogen bromide were added and the refluxing was continued.

400 g. of trimethylene glycol and 1800 cc. of 48% aqueous hydrobromic acid were placed in a 4-liter flask and refluxed on a sand bath 3–4 hrs., when 850–900 g. of gaseous hydrogen bromide were introduced.

The hydrogen bromide was generated by dropping bromine upon a mixture of red phosphorus, water and sand, and purified by passing over moist red phosphorus spread over glass wool in U-tubes. A convenient charge was found to be 1600 g. of sand, 300 cc. of water, 200 g. of red phosphorus, and 1200 g. of bromine. With this apparatus it required but 2–3 hours to generate the amount of hydrogen bromide desired in this case.

The mixture was gradually brought to boiling and refluxed again for two hours in order to establish the equilibria. Upon cooling, the bromide completely separated from the solution. This was isolated and washed with water, sulfuric acid and carbonate solution as in the preceding experiment. The product, after drying with $CaCl_2$, distilled constant at 165°. The yield was 870 g. or 82% theoretical, as compared to 53% by the preceding method.

An amount of 48% hydrobromic acid, equivalent to the amount used, is regained by distilling the aqueous layer.

3. **γ-Bromobutyronitrile.**—*Gabriel's Method.*—Gabriel[1] prepared this substance from trimethylene bromide and potassium cyanide in the usual solvent, a mixture of ethyl alcohol and water. Obviously the main reactions are

[1] *Ber.*, **22**, 3336 (1889).

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$$BrCH_2.CH_2.CH_2Br + KCN \longrightarrow BrCH_2.CH_2.CH_2CN + KBr$$
$$BrCH_2.CH_2.CH_2CN + KCN \longrightarrow NC.CH_2.CH_2.CH_2CN + KBr$$

The yield of the γ-bromobutyronitrile was only 19%, and but 40% of the trimethylene bromide used was accounted for in the products of the reaction. This method was repeated in the present investigation with but little better results, as shown in Table V.

The poor yield may be due to the presence of water. Since the aqueous solution becomes alkaline by the hydrolysis of potassium cyanide, a large number of hydrolytic products would be expected. At the end of the reaction, the aqueous layer was actually found to turn congo-red paper blue, proving the presence of a strong acid. Some of the types of these hydrolytic reactions which might occur are shown by the following equations:

$$BrCH_2.CH_2.CH_2Br + H_2O \rightleftharpoons BrCH_2.CH_2.CH_2OH + HBr$$
$$BrCH_2.CH_2.CH_2CN + H_2O \rightleftharpoons BrCH_2.CH_2.CH_2CO.NH_2$$
$$BrCH_2.CH_2.CH_2CO.NH_2 + H_2O \rightleftharpoons BrCH_2.CH_2.CH_2COOH + NH_3$$
$$NC.CH_2CH_2.CH_2CN + H_2O \rightleftharpoons NC.CH_2.CH_2CH_2CO.NH_2$$
$$NC.CH_2.CH_2.CH_2CO.NH_2 + H_2O \rightleftharpoons NC.CH_2.CH_2.CH_2COOH + NH_3$$
$$NC.CH_2.CH_2.CH_2COOH + H_2O \rightleftharpoons H_2N.OC.CH_2.CH_2.CH_2.COOH$$
$$H_2N.OC.CH_2.CH_2.CH_2COOH + H_2O \rightleftharpoons HOOC.CH_2.CH_2.CH_2.COOH + NH_3$$

Method II.—In the light of above considerations it is obvious that an anhydrous solvent might be preferable. Since methyl alcohol dissolves 5% of potassium cyanide at 0° it was chosen as the solvent for this reaction. Another important factor to be considered is the relative proportions of trimethylene bromide and potassium cyanide. An excess of the bromide should favor the yield of γ-bromobutyronitrile and decrease the yield of the trimethylene cyanide. Table V confirms this and shows the advantage of the use of anhydrous methyl alcohol as the solvent.

TABLE V.—ACTION OF POTASSIUM CYANIDE UPON TRIMETHYLENE BROMIDE.

Method.		G. material used.			G. products.		
		Solvent.	Potassium cyanide.	Trimethylene bromide.	Trimethylene bromide, 70–72°, 20 mm.[1]	γ-Bromobutyronitrile, 100–102°, 20 mm.[1]	Trimethylene cyanide, 148–153°, 20 mm.[1]
I	a	C_2H_5OH 95%, 450	60	200	20	27	10
	b	H_2O, 120	65	202	15	39	14
II	a	CH_3OH 1000	65	200	32	44	20
	b	CH_3OH 1000	65	404	175	70	4

In both cases under Method II the materials were mixed together and refluxed on the steam bath 7–8 hours. The potassium bromide was fil-

[1] The temperature readings in this table are not corrected.

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tered off and the alcohol was distilled from the mixture. The residue was separated into its components by fractional distillation under reduced pressure.

The methyl alcohol was that of Eimer and Amend freshly refluxed over and distilled from an excess of good lime. The trimethylene bromide was prepared as described in the preceding section. Eimer and Amend's 98–100% potassium cyanide was used.

Discussion of Table V.—The first horizontal column, Method I*a*, gives the results obtained by Gabriel. Method I*b* shows the results of the repetition of his method in this laboratory. A comparison of this with Method II*a* discloses, to some extent, the hydrolytic effect of the water present. Although the yield of γ-bromobutyronitrile is not appreciably greater with the use of methylalcohol, twice the amount of trimethylene bromide is recovered and half as much again trimethylene cyanide is obtained. The most striking advantage is shown by the use of an excess of trimethylene bromide in Method II*b*. When one mole each of trimethylene bromide and KCN were used in Method II*a*, only 44 g. of γ-bromobutyronitrile while 20 g. of trimethylene cyanide were obtained also. The use of two moles of trimethylene bromide to one of potassium cyanide gave 70 g. of γ-bromobutyronitrile and only 4 g. of trimethylene cyanide. The excess of trimethylene bromide is easily recovered in the distillation.

4. **δ-Cyano-α-acetovalerianic Ethyl Ester.**—This substance is not described in the literature. For the present purpose it was prepared by the action of γ-bromobutyronitrile on the sodium salt of acetoacetic ethyl ester with absolute ethyl alcohol used as the solvent. The principal reactions predicted are

$$\underset{\underset{\displaystyle O}{\|}}{CH_3C.CH_2.COOC_2H_5} \rightleftharpoons \underset{\underset{\displaystyle OH}{|}}{CH_3C{:}CHCOOC_2H_5} \quad (1)$$

$$\underset{\underset{\displaystyle OH}{|}}{CH_3C{:}CHCOOC_2H_5} + NaOC_2H_5 \rightleftharpoons \underset{\underset{\displaystyle ONa}{|}}{CH_3C{:}CHCOOC_2H_5} + HOC_2H_5 \quad (2)$$

$$\underset{\underset{\displaystyle ONa}{|}}{CH_3C{:}CHCOOC_2H_5} + Br(CH_2)_3CN \longrightarrow \underset{\underset{\displaystyle O}{\|}}{CH_3C.\overset{\overset{\displaystyle CH_2CH_2CH_2CN}{|}}{C}HCOOC_2H_5} + NaBr. \quad (3)$$

$$\underset{\underset{\displaystyle O}{\|}}{CH_3C.\overset{\overset{\displaystyle CH_2CH_2CH_2CN}{|}}{C}HCOOC_2H_5} \rightleftharpoons \underset{\underset{\displaystyle OH}{|}}{CH_3C{:}\overset{\overset{\displaystyle CH_2CH_2CH_2CN}{|}}{C}.COOC_2H_5}. \quad (4)$$

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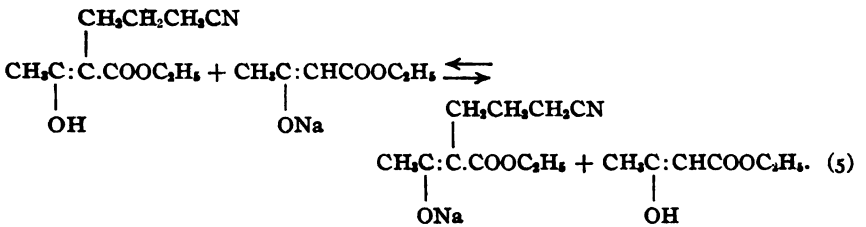
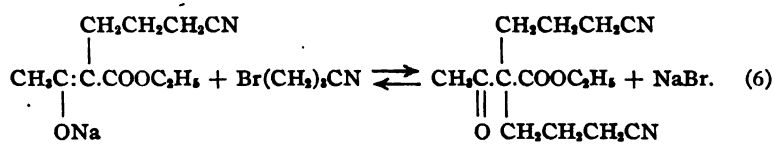


(5)



(6)

From a consideration of these equations it was predicted that some 1,7-dicyano-4-aceto-4-carboxethyl heptane would be formed by Equations 5 and 6 at the expense of the desired product, δ-cyano-α-aceto-valerianic ethyl ester by Equation 3 and, consequently, some aceto-acetic ester would remain unchanged. Everyone who has made the aceto-acetic ester condensation will recall that even when the calculated quantity of the ester is used some of it is usually regained from the products of the reaction. It follows that an excess of acetoacetic ester should displace equilibrium 5 to the left and thus decrease the yield of the undesired product. These predictions were decidedly substantiated in the two following experiments:[1]

The γ-bromobutyronitrile used in both cases was that prepared as described in the preceding section. The acetoacetic ester was made in the summer preparation work conducted at the University of Illinois. The alcohol was made absolute by twice refluxing the 95% product over an excess of good lime for several hours and distillation from the steam bath.

In both cases the procedure for making the condensation was identical. The only variable was the amount of acetoacetic ester used. The alcoholic solution of the sodium salt of acetoacetic ester was prepared in the usual manner. During the addition of acetoacetic ester to the sodium alcoholate, precautions were taken to keep the solution cool. The halide was added and the mixture was refluxed on the steam bath 7 hours. At the end of this time the sodium bromide was filtered off and the alcohol was distilled from the product. The residue was distilled under diminished pressure. The quantitative results are given in the following table:

[1] It is further interesting to note that in every tautomeric condensation some of the initial tautomer may be recovered due to equilibria of type 5, and the resulting formation of an equivalent amount of the di-alkyl compound simultaneously with the mono-alkyl compound.

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TABLE VI.—REACTIONS BETWEEN ACETOACETIC ESTER AND γ-BROMOBUTYRONITRILE.

Experiment No.	G. material used. Alcohol.	Sodium.	γ-Bromobutyronitrile.	Acetoacetic ester.	G. products. Acetoacetic ester, 80–82°,[1] 20 mm.	δ-Cyano-δ-acetovalerianic ethyl ester, 153–155°,[1] 3 mm.	1,7-Dicyano-4-aceto-4-carboxethyl heptane, 200–205°,[1] 3 mm.
I	80	8.5	55	48	5	45 (66%)	9
II	80	8.5	55	72	24	60 (82%)	1

It will be observed that equivalent quantities of materials were used in Expt. I while 1.5 equivalents of acetoacetic ester were used in Expt. II. It is seen that the production of the undesired product is almost entirely eliminated in the latter case. The advantage of a thorough consideration of mass action is obvious.

That Fraction II, Table VI, is δ-cyano-α-acetovalerianic ester is proven by its method of synthesis and its hydrolysis to δ-acetovalerianic acid as described in a following section. Because of superheating it was found difficult to determine accurately the boiling point of this substance under diminished pressure. It is approximately 154° under 2 mm. Under ordinary pressure it decomposes before the boiling point is reached. The odor of the product obtained was unpleasant but this may have been due to a trace of impurities. It is a colorless, viscous liquid soluble in most organic solvents.

5. 1,7-Dicyano-4-aceto-4-carboxethyl Heptane. Di(γ-cyanopropyl)-acetoacetic Ethyl Ester.—That Fraction III, Table VII, in the preceding section, is 1,7-dicyano-4-aceto-4-carboxethyl heptane has been established by the following considerations: In the first place the synthesis predicts its formation. The redistillation of this fraction gave a product boiling at approximately 200° under 5 mm. pressure. The distillate was a viscous and slightly yellowish liquid which crystallized very slowly. The solid was washed with ether and sucked dry on the filter. The product was colorless, possessed a pleasant, nutty color and melted sharply at 76.5°. A nitrogen determination was made by the Dumas method.

Calc. for $C_{14}H_{20}O_3N_2$: N, 10.6%. Found: N, 9.1%, 9.5%.

These are not good checks but a consideration of the possible products makes it very probable that it is the substance named above. The structure of this substance is further confirmed by hydrolysis. 1.3 g. were refluxed with constant boiling aqueous hydrochloric acid 6–7 hours. A gas was evolved, which with lime-water gave a precipitate effervescing when treated with dilute acid. This indicates the loss of a carboxethyl group from the initial substance. The acid liquors were made alkaline with sodium carbonate, extracted with benzene and then with ether in order to remove any unchanged nitrile. After acidification with hydro-

[1] As in Table V these temperatures are not corrected.

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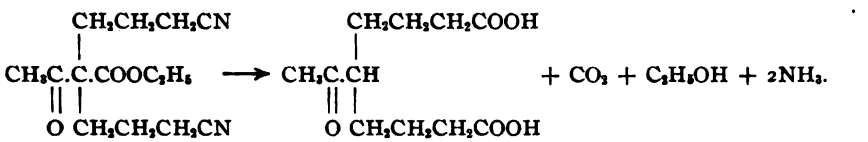
chloric acid the solution was extracted three times with ether and dried with anhydrous sodium sulfate. The evaporation of the ether left a small amount of a viscous liquid which could not be made to crystallize. This was placed in an evacuated desiccator over soda lime for several days. With dilute acid 1,7-dicyano-4-aceto-4-carboxethyl heptane should give δ-acetoazelaic acid, a substance which is not described in the literature, but its neutrality equivalent is 115.05. The product obtained possessed an equivalent of 115.5. The reaction equation is



1,7-Dicyano-4-aceto-4-carboxethyl heptane is colorless and has a pleasant, nutty odor. It boils at approximately 200° under 5 mm. pressure, bath 290°; melting point, 73.5°. It is very sparingly soluble in alcohol, ether, carbon disulfide, chloroform, petroleum ether and water, but appreciably soluble in benzene.

6. δ-Acetovalerianic Acid and Its Sodium Salt.—δ-Cyano-α-acetovalerianic ester hydrolyzes almost quantitatively to δ-acetovalerianic acid with the constant boiling hydrochloric acid mixture.

The best results were obtained by using the ratio of about 20 g. of ester to 100 cc. of 20% hydrochloric acid. Although the ester dissolved in less than thirty minutes when the mixture was boiled, the solution was refluxed several hours longer. After cooling it was neutralized with sodium carbonate and was extracted with ether until a portion left no residue when dried with sodium sulfate and the ether was evaporated. It was next made distinctly acid to congo-red by the addition of hydrochloric acid and was repeatedly extracted with ether. This required 10–15 extractions of 25–30 cc. each. This number can be greatly reduced by salting out with ammonium sulfate. The ether solution was dried with sodium sulfate, the ether was evaporated and the residue was distilled under low pressure.

It was desired to obtain this acid in a state of absolute purity for conductivity measurements. Toward this end it was first distilled under different pressures. A fraction which boiled constant at 135° under about one mm. pressure was collected. This distilled at 181–182° under 25 mm.

This portion was next converted into the sodium salt. Instead of making it in the usual manner of precipitation from an alcoholic solution with

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sodium hydroxide, an equivalent amount of metallic sodium dissolved in absolute alcohol was employed. The advantages considered were the absence of water and the greater ease of solution of the sodium. 1.8 g. of sodium were dissolved in 200 cc. of absolute alcohol. To the hot solution 11.5 g. of the acid were gradually added. A small amount of insoluble material was filtered off. Upon cooling, the entire solution solidified to a mass of the consistency of a cake of moist soap. This product was sucked as dry as possible on a Büchner filter, using a hardened filter paper and washed three times with absolute ether. The filtrate was concentrated and treated in the same manner, this precipitate being added to the other. This process was repeated with two more portions of alcohol of about the same volume. The salt was dried in an electric oven at 90–100° for 4 hours, pulverized in an agate mortar and placed in a $CaCl_2$ evacuated desiccator overnight. The product was white and fluffy. The amount of sodium was determined by the sulfate method.

Calc. for $C_7H_{11}O_2Na$: Na, 13.85%. Found: Na, 13.85%, 13.84%.

The conductivity data of this salt will be found in a following section.

In order to recover the pure acid, 15 g. of this salt were dissolved in 50 cc. of water and 10 cc. of hydrochloric acid (sp. gr. 1.19, 37%) diluted with an equal volume of water, were added while the whole was kept cool. This solution was extracted twelve times with 20 cc. of alcohol-free ether and dried over sodium sulfate for several hours. After the evaporation of the ether and the reduction of the pressure at the beginning of the distillation a few drops of water came over. This suggests the formation of a hydrate. During the second distillation a fraction boiling at 160° under 13 mm., bath 235°, was collected. This was cooled in an evacuated $CaCl_2$ desiccator and pulverized in an agate mortar. Its neutrality equivalent was obtained by titration with standard barium hydroxide solution.

Calc. for $CH_3CO.(CH_2)_4COOH$: 144.1. Found: 143.8, 143.7.

The acid purified in the above manner melts sharply at 36.5°. Here again, because of the tendency to superheat, it was difficult to determine accurately the boiling points under reduced pressure. They were found to be approximately 135° at 1 mm. pressure, bath 195°, and 181° at 25 mm., bath 245°. The ionization constant is 1.926×10^{-5}. The data for the determination of this are given in the following sections.

Other investigators have reported the preparation of δ-acetovalerianic acid, but not by the above method. In all cases the product was of questionable purity. W. H. Perkin[1] reported its melting point at 40–42°. The yield was not stated. The acid could not be obtained, in more than a trace, by his method in the present case. In one investigation Wal-

[1] *J. Chem. Soc.*, **57**, 230 (1890).

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lach[1] states that he obtained this acid with a melting point of about 50°. By another method this investigator[2] obtained the same product with a melting point at 38–40°. Wallach thought that tautomerism or hydration might be interfering. Blaise and Koehler[3] gave its melting point at 31–32°. Thus it is seen that the melting points reported range from 31 to 50° as compared to the one at 36.5°, sharply, obtained in this investigation.

VII. Electrical Conductivity Measurements.

1. Method and Apparatus.—The method and apparatus used were those described by Derick and Kamm,[4] with the exception that a cell with platinized electrodes was used for measuring the conductivity of the acid. Its constant was 0.06233. A cell of about the same size with unplatinized electrodes and with a constant of the value 0.06776 was employed for the salt. A cell of about twice the size but of the same type with a constant 0.02952 was used for determining the conductance of the water.

2. Preparation of Solutions and Procedure of the Measurements.—The conductivity water was prepared as described by Derick and Kamm.[4] The solutions were prepared on the basis of one equivalent to 1000 g. of solution. Because of the extreme dilution this should cause no appreciable error.

For each concentration 300–400 g. of solution were prepared. They were weighed on a large balance to an accuracy of a few hundredths of one per cent. Both acid and salt were weighed in an ordinary weighing tube. Care was taken to allow the balance to come to equilibrium before the final weights were taken. Since the acid is somewhat hygroscopic, it was never poured from the weighing tube into a wet flask and it was exposed to the air as briefly as possible.

3. Symbols Used for Conductivity Data.—The symbols used for the conductivity data have the following meanings:

C = Moles of solute per 1000 g. of solution.
L = Specific conductance in reciprocal ohms.
Λ = Equivalent conductance at a given concentration.
Λ_0 = equivalent conductance at infinite dilution.
k = Ionization constant calculated from the Ostwald dilution law,

$$k = \frac{C\Lambda^2}{\Lambda_0(\Lambda_0 - \Lambda)}.$$

These same symbols with the subscript c means that they have been corrected for the conductance of the water by the subtraction of the

[1] *Ann.*, 329, 377 (1903).
[2] *Ibid.*, 359, 309 (1908).
[3] *Compt. rend.*, 148, 490 (1909).
[4] THIS JOURNAL, 39, 392 (1917).

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total specific conductance of the water from the specific conductance of the solution of the electrolyte.

All data is given at the temperature of 25° ± 0.01°.

4. Conductance and Ionization Constant of δ-Acetovalerianic Acid.—The acid used was that prepared in a very high degree of purity as described in Section **VI-6**. The value for the specific conductance of the water is 0.60×10^{-6}.

TABLE VII.

δ-Acetovalerianic Acid. Temperature, 25.00 ± 0.01°.

C.	$L \cdot 10^{-4}$.	$L_c \cdot 10^{-4}$.	Λ.	Λ_c.	$k \cdot 10^{-5}$.	$k_c \cdot 10^{-5}$.
0.02	2.298	2.292	11.49	11.46	1.926	1.917
0.01	1.614	1.608	16.14	16.08	1.924	1.910
0.0075	1.393	1.387	18.58	18.49	1.927	1.907
0.005	1.131	1.125	22.62	22.50	1.926	1.904
0.0025	0.7900	0.7840	31.60	31.36	1.928	1.898
0.001	0.4872	0.4812	48.72	48.12	1.928	1.877

By the Ostwald[1] and the salt method, the data given in the next section give the value 376 for Λ_0 of this acid. The values 51.2 and 347.2 were used for the equivalent conductances of the sodium and hydrogen ions, respectively, at infinite dilution.

It will be observed that the values for the ionization constant, calculated from the uncorrected conductances, check each other to an accuracy of 0.1%, while those calculated from the corrected conductances gradually decrease in value with increasing dilution. It is generally agreed, however, that the total specific conductance of the water should not be subtracted from the specific conductance of the solution as has been done in this case. The application of "calculated" Λ_0 (Section **VII-6**) shows that the correction should not have been made in this manner. Kendal[2] has recently summarized the investigations made in this field and has shown that the *true* correction is insignificant, for acids stronger than acetic, if the water conductance is due to carbon dioxide only. The care which was taken in preparing the conductivity water and the solutions in the present case makes it highly probable that the only impurity was carbon dioxide. "Calculated" Λ_0 is shown to confirm this probability.

The conclusion is drawn from these considerations that the ionization constant of δ-acetovalerianic acid is $1.926 \pm 0.002 \times 10^{-5}$ at 25°.

5. Conductance Measurements on the Sodium Salt of δ-Acetovalerianic Acid.—The salt used was that prepared in a high degree of purity as previously described (Section **VI-6**). The specific conductance of the water was 0.926×10^{-6}.

[1] Lundén's "Affinitätmessungen an schwachen Säuren und Basen," *Sammlung Chemischer und tech. Vortrage*, 14, 9 (1909).

[2] THIS JOURNAL, 39, 7 (1917).

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TABLE VIII.

Sodium Salt of δ-Acetovalerianic Acid. Temperature, 25.00 ± 0.01°.

C.	L_c.	Λ_c.	$1/\Lambda_c$.	$(C\Lambda_c)^{0.45}$.	$\sqrt[3]{C}$.
0.01	0.0007155	71.55	0.01397	0.8601	0.2154
0.0075	0.0005433	72.44	0.01380	0.7599	0.1957
0.005	0.0003673	73.46	0.01361	0.6312	0.1710
0.0025	0.0001776	75.06	0.01332	0.4710	0.1357
0.001	0.00007645	76.45	0.01308	0.3144	0.1000
0.00075	0.00005774	76.98	0.01299	0.2771	0.09085
0.0005	0.00003896	77.92	0.01283	0.2322	0.07937
0.00025	0.00001955	78.20	0.01278	0.1703	0.06999
0.0001	0.000007929	79.29	0.01261	0.1134	0.04642

The value 80 was obtained for Λ_0 of the salt by two different methods of plotting the conductance data. One was the usual method of plotting $(C\Lambda_c)^{0.45}$ against $1/\Lambda_c$; in the other case $\sqrt[3]{C}$ was plotted against Λ_c.[1] The above value for Λ_0 was obtained by extrapolating a straight line through the points in each case. The necessary data is given in Table VIII.

6. The Application of "Calculated" Λ_0 to the Conductance Data of δ-Acetovalerianic Acid.—The criterion "calculated" Λ_0[2] has been applied to the conductance data of this acid corrected and uncorrected for the conductance of the water and recorded in Table IX. The uncorrected conductances (Λ, Table VII) were employed in making the calculations in Col. I; the corrected conductances (Λ_c, Table VII) in Col. II.

TABLE IX.—δ-ACETOVALERIANIC ACID.

Concentration.	I. "Calc." Λ_0.	II. "Calc." $\Lambda_{0(c)}$.
0.02 and 0.01	369	308
0.0075	383	307
0.005	370	319
0.0025	381	323
0.001	379	321
0.01 and 0.0075	413	305
0.005	370	321
0.0025	385	327
0.001	381	323
0.0075 and 0.005	350	331
0.0025	381	331
0.001	379	324
0.005 and 0.0025	397	331
0.001	383	323
0.0025 and 0.001	377	319

The values of "calculated" $\Lambda_{0(c)}$ are seen to be much lower than the value 376 obtained by the salt method. This shows the presence of a

[1] Kohlrausch und Holborn, "Leitvermögen der Elektrolyte," p. 107.

[2] Derick, THIS JOURNAL, 36, 268 (1914).

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constant error, produced by subtracting the total conductance of the water from that of the solution of the acid. This is to be expected if the conductance of the water is due to the presence of carbon dioxide only.

On the other hand, the values of "calc." Λ_0 are seen to be much closer to but slightly higher than 376. This indicates that a small constant error is involved somewhere. It is probably due to the slight conductance of carbon dioxide. However, the agreement is quite satisfactory considering the extreme sensitivity of the criterion. In order to appreciate this statement one should review the values of "calculated" Λ_0 applied by Derick[1] to the measurements on acetic by Ostwald, Jones, Van't Hoff and Kendall, where the deviations are much greater. The sensitivity of this criterion is also brought out in the application to Franke's and to Drucker's measurements of normal heptanoic acid (Section VIII).

The conclusion drawn from these considerations is that the conductance of the water is due to carbon dioxide and, consequently, no correction should be applied to the conductance of the acid for the desired accuracy of 0.1% in the ionization constant.

VIII. The Ionization Constant of, and the Application of "Calculated" Λ_0 to the Conductance Data of, Normal-Heptanoic Acid.

Different values for the conductances and the ionization constant of normal heptanoic acid have been found by Franke[2] and Drucker.[3] In order to obtain more accurate values, it was necessary to correct the conductances at the concentrations given by Franke to reciprocal ohms. His value of Λ_0 for the acid, corrected to reciprocal ohms and to the values 51.2 and 347.2 for the equivalent conductances of the sodium and hydrogen ions, respectively, at infinite dilution, was found to be 377. It was only necessary to correct Drucker's value for Λ_0 of the acid for the conductances of the sodium and hydrogen ions. 377 was obtained in this case also. The corrected conductances and ionization constants of both investigators are given in Table X.

TABLE X.—NORMAL HEPTANOIC ACID.

Franke.			Drucker.		
v.	$\Lambda_{(?)}$.	$k_{(?)}\cdot 10^{-5}$.	C.	Λ_c.	$k_c\cdot 10^{-5}$.
128	15.02	1.29	0.01103	13.17	1.40
256	21.00	1.28	0.005515	18.13	1.34
512	29.41	1.29	0.002760	26.00	1.40
1024	40.56	1.27	0.001380	36.30	1.41

It was not stated whether or not the conductance data of Franke was corrected for the conductance of the water.

The application of "calculated" Λ_0 to both sets of measurements are given in Table XI.

[1] THIS JOURNAL, 36, 268 (1914).
[2] *Z. phys. Chem.*, 16, 463–92 (1895).
[3] *Ibid.*, 52, 641–704 (1905).

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TABLE XI.—APPLICATION OF CALCULATED Λ_0.

Franke.		Drucker.	
Concentrations.	"Calc." Λ_0 (?).	Concentrations.	"Calc." Λ_0 (?).
128 and 256	280	0.01103 and 0.005515	108
512	362	0.002760	531
1024	304	0.001380	480
256 and 512	456	0.005515 and 0.002760	—251
1024	311	0.001380	—5812
512 and 1024	257	0.002760 and 0.001380	434

The presence of constant errors is disclosed in the measurements by Franke. From a consideration of the equations

$$\frac{dk}{k} = \frac{2\Lambda_0 - \Lambda}{\Lambda_0 - \Lambda}\left(\frac{d\Lambda}{\Lambda}\right) \quad \text{and} \quad \frac{d\Lambda_0}{\Lambda_0} = a\frac{d\Lambda}{\Lambda} + b\frac{d\Lambda_1}{\Lambda^1},$$ [1]

it follows that if "calculated" Λ_0 is uniformly less than the value determined by the salt method, the value of the ionization constant found, will be less than the correct one, and *vice versa*. Obviously, Franke's value for the ionization constant of normal heptanoic acid is too small. The measurements of Drucker are seen to lack precision and the ionization constant is probably a little large. Therefore, 1.4×10^{-5} is chosen as the approximate ionization constant of this acid.

IX. Summary.

1. Wegscheider's criticism of Derick's *place factor* and *rule of thirds* has been shown to be misleading. His suggestion for the use of the logarithm of the Ostwald factor concedes the very point of Derick's contention and demonstrates his error in stating that Derick and his students have not advanced the problem of the correlation of ionization and structure.

2. The ionization constants of several organic acids have been recalculated from conductances corrected to reciprocal ohms and for the recently determined conductances of the sodium and hydrogen ions.

3. The theoretical basis for the measurement of the *place influence* of substituents upon the ionization of organic acids has been developed.

4. The relative ϵ-place influence of the divalent oxygen atom, upon the ionization of paraffin monobasic acids, has been found to be approximately 0.14.

5. A convenient and efficient method for making pure trimethylene bromide on a large laboratory scale has been presented. A modified Norris method increases the yield 30%. 82% of the trimethylene glycol is converted into this bromide. The advantage of applying the collision method of study and mass action is demonstrated.

6. The use of methyl alcohol as a solvent, instead of the customary mixture of ethyl alcohol and water, for making γ-bromobutyronitrile

[1] Derick, THIS JOURNAL, 36, 2270–2271 (1914).

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from trimethylene bromide and potassium cyanide has been shown to be advantageous. This alcohol is suggested as a general solvent for making nitriles especially where there is danger of hydrolysis. Here again the yields are increased by the application of the collision method of study and mass action to the chemical equilibria involved.

7. It has been found that when γ-bromobutyronitrile is treated with one equivalent of aceto acetic ester two products result: one, γ-cyano-α-acetovalerianic ethyl ester, a combination of one molecule of each; the other, 1 : 7-dicyano-4-aceto-4-carboxethyl heptane, composed of one molecule of the ester and two of the nitrile. When 1.5 equivalents of aceto-acetic ester were used the latter was suppressed to one-ninth of the amount produced when one equivalent was used. This result was predicted from a consideration of the principle of mass action.

8. Two new substances, δ-cyano-α-acetovalerianic ethyl ester and 1,7-dicyano-4-aceto-4-carboxethyl heptane have been prepared and characterized.

9. δ-Acetovalerianic acid has been prepared in a pure state and in large quantities for the first time. Its ionization constant is $1.926 \pm 0.002 \times 10^{-5}$. The application of "calculated" Λ_0 proves this value to be accurate. Its correct capillary melting point is 36.5°.

10. The electrolytic conductance of the sodium salt of δ-acetovalerianic acid has been determined for a series of concentrations and the extrapolated Λ_0 value found to be 80.

11. The application of "calculated" Λ_0 to the existing conductance data of normal heptanoic acid shows that it is very inaccurate.

URBANA, ILL.

[CONTRIBUTION FROM THE LABORATORIES OF THE INLAND REVENUE DEPARTMENT.]

THE MANGANESE CONTENT OF THE ASH OF CERTAIN DRUGS.

BY L. E. WESTMAN AND R. M. ROWAT.

Received December 18, 1917.

Although the significance of the presence of manganese in plants and its relation to plant metabolism is not yet clear, the quantity of manganese observed to be present in the barks of certain laxative drugs and in other portions of plants used for similar purposes, was considered by the authors to be worthy of general mention.

Hafner and Krist[1] have pointed out in a qualitative way that a large number of drug plants contain manganese. They were able to obtain positive tests for manganese on 164 drugs listed in the Austrian Pharmacopeia, and were led to this investigation by the occurrence of a greenish color in the ash of many drugs. This color is formed when the ash is

[1] *Z. Osterr. Apoth. Ver.*, **45**, 387–399 (1907).

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strongly heated in a muffle, from the manganite salts present and is certainly most marked in many instances, especially those where an extract of the drug has been evaporated and ashed. This is due to the fact that only a small fraction of the lime salts present in plants is extracted by methods of percolation, and in the relative absence of these salts the manganese that is extracted becomes observable in the ash.

The method adopted by these authors in their tests was as follows: 3 to 4 g. samples of the drug were ashed and the ash dissolved in 8 to 10 cc. of dilute nitric acid (free from hydrochloric acid), filtered if necessary, then heated, and after the addition of a small amount of brown, manganese-free lead peroxide, was brought to boiling. When manganese was present the liquid acquired a more or less intense purple-red color according to the amount. This reaction naturally fails in the presence of chlorides.

According to Pichard,[1] the seeds of plants are quite rich in manganese, and Jadin and Astruc[2] find that the aerial portions of plants contain more manganese than the subterranean. McHargue[3] tabulates 51 determinations made on nuts, shells, seeds, and seed coatings, obtaining for his two highest results 0.04% manganese in dried potato peelings, and 0.09% in dried turnip tops. Manganese has been shown by Headden[4] to be present in all samples of wheat examined in amounts from 0.004 to 0.007%.

Results and Discussion.

The results obtained are tabulated below and are calculated on the dry basis at 110°:

TABLE I.

Drug examined.	% manganese present.	
Rhamnus Frangula (or alder buckthorn bark)	0.0242 to 0.0674	±0.0003
Cinnamomum Cassia Cortex (or cassia bark)	0.0624	±0.0003
Rhamnus Purshiana (cascara sagrada)	0.0137 to 0.0223	±0.0003
Podophyllin (root)	0.0052	±0.0002
Senna (leaves)	0.0043	±0.0002
Rhubard (root)	0.0036	±0.0002
Rhamnus Californica (mature bark)	0.0033	±0.0002
Licorice (root)	0.0026	±0.0001
Jalap (root)	0.0024	±0.0001
Euonymus Atropurpureus (wahoo bark)	0.0021	±0.0001
Cassia pulp	0.0017	±0.0001
Aloes (barbadoes)	0.0006	±0.00005

From data available it would appear that both *Rhamnus Frangula* and cassia bark show a higher content of manganese than any other

[1] P. Pichard, *Compt. rend.*, **126**, 1882 (1898).
[2] Jadin and Astruc, *Ibid.*, **156**, 2023 (1913).
[3] J. S. McHargue, THIS JOURNAL, **36**, 2532 (1914).
[4] W. P. Headden, *J. Agr. Res.*, **5**, No. 8, 349 (1915).

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similar plant tissue previously examined. It was found that all samples of these barks did not show the same manganese content, and observed limits of the amounts present are given above. The lower numbers represent mature or thick bark while the higher numbers were obtained from thinner bark. It is quite possible that an examination of specially selected bark would widen this range, but the work reported was carried out on various samples and it is thought that it covers the range fairly well. Factors involving the change of manganese content with the season have not, however, been studied. In an attempt to locate the cells or region of the bark giving the highest content of manganese, both inside and outside scrapings were examined. It was found for *Rhamnus Purshiana* that the concentration of manganese in the inner third of the bark was about double that present in the outer third. This may indeed be generally true and would go to show that although manganese is present in the outer layers of the bark it really functions more particularly in the inner layers where plant metabolism is more actively going on. The accidental presence of definite amounts of manganese in these barks cannot be accepted as an explanation, while the conception that a definite concentration of manganese is a factor in the normal metabolism of any particular species, seems more probable. It is natural to expect that a plant using a higher concentration of manganese in certain working cells might leave behind in the older bark a higher uniform residue. In any case it seems evident that definite amounts of manganese may be found present in all or any of the different parts of plants.

Manganese Fraction Soluble in Water.

By methods of percolation, and by boiling the powdered barks in water, it was found that about one-quarter of the total manganese present may be extracted from members of the *Rhamnaceae* family by this means.

TABLE II.

Bark examined.	Total manganese in the bark.	Manganese extracted.[1]
Rhamnus Frangula	0.0242%	0.0058%
Rhamnus Purshiana	0.0137	0.0029
Rhamnus Californica	0.0033	0.0008

The numbers are based on dry samples as above and are the average results of several good duplicate determinations, showing the uniformity with which manganese is extracted from such materials. Manganese thus extracted does not appear to have the properties of inorganic manganese and is not removed from these solutions by ordinary means. This at once leads to a new method for distinguishing between these closely related species and it follows from this that the development of a "Manganese Number" for commercial extracts of such drugs would seem to be a quite

[1] U. S. P. type process D, p. 176 (1910).

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reasonable and practical method of procedure in their examination. It is our hope to develop such an application in the near future.

Method of Estimation.

The analytical work reported was accomplished by a simple application of the ammonium persulfate method for the determination of small amounts of manganese. The work was done in two ways, depending on the manganese found present by initial trials.

Wherever 10 g. samples are available, the following procedure may be recommended: If the presence of manganese is known to be of the order of 0.015% or higher, it is possible to titrate directly the permanganate formed with standard sodium arsenite solution. If the percentage is lower than this it is more feasible to compare the color developed with solutions of known permanganate content which have been carefully prepared and correspond with the unknown solution with regard to acidity and general ion concentration.

In cases of the first order of manganese content, 10 g. samples of the well-ground materials were ashed in platinum in a muffle and 20 cc. of pure concentrated sulfuric acid was added. The sample was then heated till the acid fumed freely in order to remove chlorides. It was then cooled and diluted with distilled water, washed out into a 500 cc. beaker and diluted to at least 300 cc. To this solution was added one cc. of a silver nitrate solution (5 g. in 100 cc.) and the whole warmed to about 80°. Approximately one g. of ammonium persulfate was gradually stirred into this solution which was then heated on the steam bath as long as the color of the permanganate deepened. By check analyses the reaction was found generally to be complete at the end of 30 minutes. The solution was, however, heated 45 minutes and allowed to cool. When cold it was rapidly titrated with sodium arsenite solution which had been standardized against known amounts of permanganate developed in the same way. Unless the dilution is sufficient a brown hydrated form of manganese will separate out after the addition of the ammonium persulfate. Where the percentage of manganese is as high as 0.06 a volume of 500 cc. is necessary when working on a 10 g. sample.

In cases where the manganese was of a lower order than 0.01% the color was developed as above from a 10 g. sample in a 200 cc. volumetric flask and compared by means of a colorimeter with standard solutions of permanganate.

Our thanks are due to Dr. J. M. Francis, of the Parke Davis Co., Detroit, Mich., for kindly supplying us with genuine samples of some of the above materials.

Summary.

1. The manganese content of certain laxative drugs has been measured along with allied species of plants.

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2. It has been found that for the family *Rhamnaceae* the manganese is extracted in water proportionally to its total amount in the bark.

3. A practical use of this determination is suggested leading to the establishment of a "Manganese Number" for extracts of these drugs.

OTTAWA, CANADA.

ON THE REACTIONS OF THE FORMAMIDINES. VII. THE CONSTITUTION OF SOME PYRAZOLE DERIVATIVES.

By F. B. DAINS AND ROLLA N. HARGER.

Received December 22, 1917.

In some previous papers it has been shown that the substituted formamidines react with compounds containing methylene hydrogen, giving rise to complexes in which the hydrogen of the methylene group has been replaced with the grouping = CHNHR.[1] In the case of ethyl-acetoacetate, there are formed derivatives of the two types

$$\begin{array}{l} CH_3CO\ C = CHNHR \\ \quad\quad\ \ |\ \ \ \

The following experimental work will show, however, that these derivatives should be regarded as pyrazole and not as pyrazolone compounds. It is evident that any proof of this constitution must show that the hydrazine reacts with the anilino-methylene grouping, = CHNHR, and not with the —COOR or —CONHR group.

m-Bromo-anilino-methylene-acetoacetanilide,

$$\begin{array}{l} CH_3COC{=}CHNHC_6H_4Br\text{-}m. \\ \quad\quad\quad\;\; | \\ \quad\quad\quad CONHC_6H_5 \end{array}$$

—Molar quantities of *m*-dibromodiphenyl-formamidine and acetoacetanilide were heated in an oil bath for two hours at 140°, using a little kerosene as a solvent. From the reaction mixture was isolated *m*-bromaniline (its benzoyl derivative melts at 135–6° and not at 120°,[1] and the above anilide, which crystallizes from alcohol in yellowish white needles, melting at 113°.

Calc. for $C_{17}H_{15}O_2N_2Br$: N, 7.81%; Br, 22.27%. Found: N, 7.90%; Br, 22.16%.

Synthesis of the Pyrazole Derivative.—The *m*-bromo-anilino-methylene-acetoacetanilide (4 g.) was dissolved in 100 cc. of alcohol. To this was added a concentrated solution of hydrazine sulfate together with the calculated quantity of sodium carbonate. The mixture was heated on a water bath for three hours, evaporated to dryness and extracted with methyl alcohol. The product dissolved by the methyl alcohol was purified by recrystallization from hot water, from which it separated in white rosets of needles, melting at 179°. It contained no bromine and gave figures on analysis corresponding to the anilide of (3)5-methyl-4-pyrazole-carboxylic acid,

$$\begin{array}{l} HC \text{———} CCONHC_6H_5. \\ \;\;\| \quad\quad\quad\;\; \| \\ N - NH - CCH_3 \end{array}$$

It is soluble in hot ethyl alcohol and in hot water, slightly soluble in benzene and readily soluble in acetone and methyl alcohol.

Calc. for $C_{11}H_{11}ON_3$: N, 20.91%. Found: 20.86%.

Had the reaction proceeded according to the Gattermann theory, there should have been obtained 4-*m*-bromo-anilino-methylene-5-pyrazolone, with only 14.3% nitrogen, which was not the case.

Acetoacet-*p*-toluide can be readily made by heating 30 g. of acetoacetic ester and 26 g. of *p*-toluidine for 3 hours at 130°. The product crystallizes from hot water in white, flat plates with a melting point of 89°.

Calc. for $C_{11}H_{13}ON$: N, 7.34%. Found: 7.53%, 7.60%.

When a mixture of 11 g. of the acetoacet-*p*-toluide, 21 g. of di-*p*-bromodiphenyl-formamidine and 10 cc. kerosene is heated for 2.5 hours at 120°, there are obtained *p*-bromoaniline and the *p*-toluide of *p*-bromoanilinomethylene-acetoacetic acid,

[1] *Ann.*, **264**, 179 (1891).

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$$\begin{array}{l} CH_3COC = CHNHC_6H_4Br, \\ \quad\;\; | \\ \quad CONHC_7H_7 \end{array}$$

which separates from hot alcohol or glacial acetic acid in white crystals with a melting point of 162°.

Calc. for $C_{18}H_{17}O_2N_3Br$: N, 7.51%; Br, 21.43%. Found: N, 7.65%, 7.48%; Br, 21.42%, 21.57%.

The above product reacts readily with hydrazine in boiling alcohol solution, yielding a compound, which contains no bromine, crystallizes from hot water in white needles melting at 179°, and which proved to be the *p*-toluide of (3)5-methyl-4-pyrazole carboxylic acid.

Calc. for $C_{12}H_{12}ON_3$: N, 19.65%. Found: 19.68%.

As a further confirmation the same pyrazole was obtained in another way. Acetoacet-*p*-toluide and diphenyl-formamidine, when heated, gave the anilino-methylene-acetoaceto-*p*-toluide,

$$\begin{array}{l} CH_3COC = CHNHC_6H_5. \\ \quad\;\; | \\ \quad CONHC_7H_7 \end{array}$$

The white crystals from alcohol melt at 162°.

Calc. for $C_{18}H_{18}O_2N_2$: N, 9.54%. Found: 9.50%, 9.60%.

This, treated in the usual manner with hydrazine, gave the same *p*-toluide of (3)5-methyl-4-pyrazole carboxylic acid (m. p. 179°), thus proving again that it is the —RNH of the =CHNHR and not of the —CONHR, that is removed.

***o*-Ethoxyanilide of Acetoacetic Acid,** $CH_3COCH_2CONHC_6H_4OC_2H_5$.—Molar quantities of acetoacetic ester and *o*-phenetidine were heated at 120–130° for 2.5 hours. The product was distilled with steam and the residue in the flask, when crystallized from gasoline, gave the above anilide, white needles which melt at 92°.

Calc. for $C_{12}H_{15}O_3N$: N, 6.49%. Found: 6.42%.

Diphenyl-formamidine condenses readily on heating with the ethoxy-anilide forming the *o*-ethoxy-anilide of anilino-methylene-acetoacetic acid,

$$\begin{array}{l} CH_3COC = CHNHC_6H_5 \\ \quad\;\; | \\ \quad CONHC_6H_4OC_2H_5. \end{array}$$

It crystallizes from alcohol in white needles with a melting point of 135°.

Calc. for $C_{19}H_{21}O_3N_2$: N, 8.65%. Found: 8.78%.

When this methylene derivative is treated with hydrazine sulfate and sodium carbonate or with hydrazine hydrate, pyrazole synthesis again occurs through loss of the anilino and not the ethoxyanilino group, and in better yield than in the previous cases. The *o*-ethoxy-anilide of (3)5-methyl-4-pyrazole carboxylic acid,

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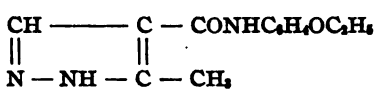


crystallizes from hot water in white needles and melts at 163°.

Calc. for $C_{12}H_{16}O_2N_2$: N, 17.15%. Found: 17.03%.

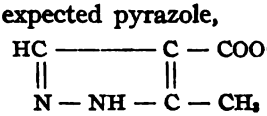
That this compound still possesses basic properties is shown by the fact that it forms a hydrochloride. This was precipitated when dry hydrogen chloride was passed into a hot benzene solution of the pyrazole. It melts with decomposition at 200°.

Calc. for $C_{12}H_{16}O_2N_2.HCl$: HCl, 12.64%. Found: 12.77%.

Di-*o*-phenetidyl-formamidine and acetoacetic ester react at water bath temperature, giving the ethyl ester of *o*-ethoxy-anilino-methylene aceto acetic acid, white crystals with a melting point of 111°.

Calc. for $C_{15}H_{19}O_4N$: N, 5.06%. Found: 4.84%.

This ester on boiling in alcohol solution with hydrazine hydrate yields a low melting solid, which could be recrystallized from hot water. The colorless needles melt at 46° and on analysis give figures which correspond to the hydrate of the expected pyrazole,



Calc. for $C_7H_{10}O_2N_2.H_2O$: N, 16.29%. Found: 16.50%.

The transparent crystals on standing in a desiccator over calcium chloride for several weeks changed to a white powder, due to the loss of water, and then melted at 54°.

Calc. for $C_7H_{10}O_2N_2$: N, 18.20%. Found: 18.27%.

That this is the ester of (3)5-methyl-4-pyrazol, carboxylic acid is also shown by the fact that when hydrolyzed it yields an acid melting at 228°. This acid had been previously obtained by Pechmann and Burkhard[1] from the action of diazo-methane upon citraconic acid, subsequent treatment with bromine and hydrolysis with concentrated hydrochloric acid.

This same pyrazole ester was also formed[2] by the action of hydrazine on 2-methyl-4-iodo-anilino-methylene-acetoacetic ester.

The 5-methyl-4-pyrazole carboxylic acid and its ester are remarkably stable towards amines, as are also its substituted amide derivatives toward hydrolysis. Thus no anilide formation was observed when the carboxylic acid or its ester was heated with aniline or *p*-toluidine at temperatures from 160–210°.

All efforts to hydrolyze the $C_4H_5N_2$-CONHR derivatives in acid or alkaline solution have thus far proved fruitless.

[1] *Ber.*, 33, 3598 (1901); THIS JOURNAL, 38, 1516 (1916).

[2] *Ibid.*, 35, 975 (1913).

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In the course of the experiments the two following compounds were prepared:

Acetoacet-*m*-bromo-anilide, $CH_3COCH_2CONHC_6H_4Br$, from acetoacetic ester and *m*-bromaniline, white plates from alcohol or hot gasoline, melting at 83°.

Calc. for $C_{10}H_{10}O_2NBr$: Br, 31.22%. Found: 31.16%, 31.17%.

The *m*-bromo-anilide of *m*-bromo-anilino-methylene-acetoacetic ester

$$\begin{array}{l} CH_3COC = CHNHC_6H_4Br \\ \quad\quad\;\; | \\ \quad\quad CONHC_6H_4Br \end{array}$$

is the main product formed on heating a mixture of acetoacetic ester and di-*m*-bromo-diphenyl-formamidine. It crystallized from alcohol in light yellow needles melting at 154°.

Calc. for $C_{17}H_{14}O_2N_2Br_2$: Br, 36.51%. Found: 36.50%.

Pyrazoles Obtained by the Action of Phenyl Hydrazine on Anilino-methylene-acetylacetone Derivatives and Their Constitution.—The substituted formamidines react with acetylacetone yielding methylene derivatives of the type $(CH_3CO)_2C = CHNHR$,[1] which condense with phenylhydrazine forming 1-phenyl-5-methyl-4-acetylpyrazole, melting at (104°) 107–8°.[2]

The pyrazole had been previously synthesized by Claison[3] from phenylhydrazine and ethoxy-methylene-acetylacetone.

Experiments with phenylhydrazine and anilino-methylene-acetylacetone confirmed the observations of Gattermann and Claison. When, however, pseudo-cumido-methyleneacetylacetone was used, not only was the above acetylpyrazole obtained, but it was accompanied by a compound melting at 175°, while *p*-toluido-methylene-acetylacetone under like conditions gave only the product melting at 175°, which proved to be the phenylhydrazone of the acetylpyrazole. The hydrazone can best be prepared as follows: A mixture of phenylhydrazine (an excess over two moles) and *o*-ethoxy-anilino-methylene-acetylacetone was warmed on the water bath for one-half hour. The contents of the flask became solid on cooling and when crystallized from alcohol gave a mass of golden yellow needles melting at 175°. The compound is difficultly soluble in cold gasoline, acetone, benzene and alcohol, very soluble in chloroform:

Calc. for $C_{18}H_{18}N_4$: N, 19.30%. Found: 19.25%.

The analysis and the following experiments indicate that the reaction has proceeded as follows: the formation of 1-phenyl-5-methyl-4-acetylpyrazole, which then reacts with a second mole of phenylhydrazine, yielding the corresponding phenylhydrazone,

$$\begin{array}{l} HC \text{———————} C.C(CH_3) = NNHC_6H_5. \\ \;\;\| \quad\quad\quad\quad\quad\quad \| \\ \;\;N - N(C_6H_5)C.CH_3 \end{array}$$

[1] *Ber.*, **35**, 2505 (1902).

[2] Gaugler and Gattermann, Dissertations, Freiburg, 1903–4.

[3] *Ann.*, **295**, 320 (1897).

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When this hydrazone is boiled with hydrochloric acid and the acid solution diluted with water, a quantitative yield of the acetylpyrazole(104°) is obtained. In fact it is the most convenient method of preparing this compound. Conversely the acetylpyrazole warmed with phenylhydrazine gives the hydrazone (175°).

Hydrazine Derivative.—Five grams of the phenyl-methyl-acetylpyrazole were dissolved in 50 cc. of absolute alcohol, together with five cc. of a hydrazine hydrate solution. The mixture was warmed for one-half hour on the water bath and then evaporated to a small bulk (6 cc.). On standing, long, four-sided prisms separated which melted at 94.5°. The new compound is very soluble in cold alcohol and in ethyl acetate, slightly soluble in benzene and readily soluble in hot gasoline. Its analysis and reactions show it to be the hydrazine derivative of 1-phenyl-5-methyl-4-acetylpyrazole,

$$\begin{array}{l} HC \text{———————} CC(CH_3)NNH_2. \\ \quad\| \qquad\qquad\qquad\quad \| \\ \quad N - N(C_6H_5) - CCH_3 \end{array}$$

Calc. for $C_{12}H_{14}N_4$: N, 26.19%. Found: 25.94%, 25.94%.

Dry hydrogen chloride precipitates from a solution of the hydrazine in benzene, a hydrochloride melting at 218°. When boiled with dilute hydrochloric acid, however, it is hydrolyzed into the original pyrazole (104°) and hydrazine. The presence of a free-NH_2 grouping is shown by the fact that it reacts readily with benzaldehyde in absolute alcohol solution giving a benzal-pyrazole azine,

$$\begin{array}{l} HC \text{———————} C - C(CH_3) = NN = CHC_6H_5. \\ \quad\| \qquad\qquad\qquad\quad \| \\ \quad N - N(C_6H_5) - C - CH_3 \end{array}$$

This forms yellow crystals from alcohol or ethyl acetate, which melt at 127°.

Calc. for $C_{19}H_{18}N_4$: N, 18.55%. Found: 18.04%.

The Azine Derivative of 1-Phenyl-5-methyl-4-Acetylpyrazole, $(C_{11}H_{12}N_2)C = NN = (C_{11}H_{12}N_2)$. — The simple pyrazole hydrazine (94.5°) can be boiled with pure ethyl acetate without change, but if a little formic or acetic acid be added and then warmed, there separates from the solvent yellow crystals melting at 174°. The same substance is slowly formed when the solution of the hydrazine in 95% alcohol is allowed to stand in the air. The acid evidently brings about a condensation of two moles of the pyrazole-hydrazine with the loss of one mole of hydrazine.

Calc. for $C_{24}H_{24}N_6$: N, 21.22%. Found: 21.41%, 21.14%.

The simple formula would be $C_{12}H_{12}N_3$, but a molar-weight determination in boiling chloroform gave 388 instead of 408, the number calculated for the formula $(C_{12}H_{12}N_3)_2$.

The azine compound (174°) on boiling with strong hydrochloric acid

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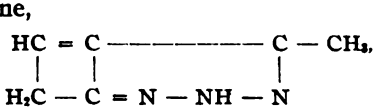
yields the original pyrazole (104°), while the solution reduces Fehling's solution, which indicate the presence of free hydrazine, since neither the original azine or the pyrazole give any reduction with that reagent.

Action of Hydrazine on the Anilino-methylene-acetylacetone.—When *o*-ethoxy-anilino-methylene-acetylacetone and hydrazine hydrate are warmed in alcohol solution, there is obtained a yellow compound melting at 320°, which is soluble in hydrochloric acid, in acetic acid and in strong sodium hydroxide, slightly soluble in aniline and nitrobenzene, but insoluble in the usual organic solvents.

The same product has been isolated by Gaugler and by Gattermann,[1] who showed in addition that it formed an ethyl and an acetyl derivative indicating the presence of an =NH group. They assigned to it the formula $C_6H_7N_3$ on the basis of the analysis and a molar-weight determination of the acetyl derivative. The provisional constitution suggested was that of a triazine,



which formulation involves the loss both of ammonia and the amine.

A more probable theory would assume that it is the azine derivative of 5-methyl-4-acetylpyrazole,

$$C_5H_8N_2C = NN = CN_2C_5H_8;\ (C_6H_8N_3)_2.$$

In favor of this hypothesis involving the double formula are the following observations: (1) It agrees equally well with the analytical data of Gaugler and Gattermann. (2) The triazine formula is an extremely improbable one. (3) Following the analogy of the phenyl-methyl-acetylpyrazole, such as azine, would be expected. (4) The azine is also capable of yielding acetyl and ethyl derivatives.

Against the azine theory is the molar-weight determination of Gaugler, indicating the single rather than the double formula, and the stability of the compound, which was boiled for six hours with strong hydrochloric acid without any evidence of hydrolysis into the hydrazine and the methyl-acetylpyrazole.

The weight of evidence, however, is in favor of the azine formula, and it is hoped that further experimental data confirming or disproving this point can be obtained later.

Summary.

1. Derivatives of 3,5-methyl-4-pyrazole carboxylic acid can be synthesized by the action of hydrazine on the amino-methylene derivatives of acetoacetic ester.

2. Phenylhydrazine yields with the anilino-methylene-acetylacetone

[1] Dissertation, Freiburg, 1903–4.

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1-phenyl-5-methyl-4-acetylpyrazole, which is capable of forming a hydrazone and azine derivatives.

3. Hydrazine and anilino-methylene-acetylacetone give an unreactive high-melting product, probably an azine.

LAWRENCE, KANSAS.

[CONTRIBUTION FROM CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY.]

STUDIES IN ESTERIFICATION. X. THE ESTERIFICATION OF BENZOIC AND THE TOLUIC ACIDS BY METHYL, ETHYL AND PROPYL ALCOHOLS.

BY RAYMOND FREAS[1] AND E. EMMET REID.

Received January 16, 1918.

Historical.

Since the work of Berthelot and Pean de St. Gilles,[2] in 1862, esterification has been one of the most frequently studied reactions. It has been regarded as one of the best examples of a reversible reaction and has been commonly used to illustrate the mass law. However, calculation of the results obtained by these workers shows that they do not agree closely with the mass law. Their work was done almost exclusively with the acids of the aliphatic series. They obtained 64.8 and 66.5% as the limits when methyl and ethyl alcohols were heated with benzoic acid in equivalent quantities, while with acetic acid the corresponding limits were 67.5 and 66.5%. Since ethyl alcohol gives sensibly the same limits with the two acids, their low result with methyl alcohol and benzoic acid seems doubtful. In fact, in a study of the interdependence of limits by Reid[3] it was assumed that methyl and ethyl alcohols give the same limits with both acids. The first object of the present investigation was to obtain accurate values for the limits of benzoic and toluic acids with methyl, ethyl and propyl alcohols. The second object was to ascertain how closely the esterification of benzoic acid by these alcohols obeys the mass law then the proportions of acid and alcohol are varied, and the third object was to study the effect of isomerism as illustrated by the three toluic acids.

Materials.

Acids.—The benzoic, *o*- and *m*-toluic acids were the commercial C. P. products; the *p*-toluic acid was made by the Sandmeyer reaction. All were purified by boiling with animal charcoal, recrystallizing several times from boiling water (diluted alcohol for the toluic acids). They were then dried for one week in a vacuum desiccator.

Alcohols.—The alcohols used were the C. P. commercial products.

[1] From dissertation of Raymond Freas.

[2] *Ann. Chim. phys.*, [3] **65**, 385 (1862); **66**, 5 (1862); **68**, 225 (1863).

[3] *Am. Chem. J.*, **45**, 479 (1911).

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They were all refluxed with quicklime or metallic calcium until density determinations showed a water content of less than 0.04%.

Esters.—The esters were prepared by usual methods and carefully purified by washing, drying and distilling.

Standard Solutions.—Standard hydrochloric acid and barium hydroxide solutions were kept in large stock bottles directly connected to the buret and protected from the air by U-tubes containing similar solutions. The barium hydroxide solution was, in addition, protected by soda lime. The solutions were very nearly 0.1 *N* and the barium solution which was most subject to change was restandardized about twice a month with the acids used in that period of time.

Glass Tubes.—The tubing used was 6 mm. in diameter, of Pyrex hard glass. Small tubes of 70 mm. length were made. These were cleaned with chromic acid solution boiled several hours in dilute hydrochloric acid and then several hours each in two changes of distilled water. They were then thoroughly dried in an air oven at 150° and kept covered to protect from dust.

Furnace.—The furnace used was an electrically heated and controlled tube furnace, similar to that described by Pratt and Reid, but of better construction. It kept the desired temperature within ± 1°.

Procedure.

The tubes were weighed, partly filled with acid or ester, drawn out and weighed again. The alcohol or water was then introduced to fill the tubes about two-thirds full. The tubes were then sealed off and the filled tube and tip weighed. Numbers scratched on the tip and the tube identified these during weighing and at titration. The tubes were then heated from 2 to 8 days at 200°, and after cooling, opened and titrated. The contents of the tubes were nearly always liquid, which necessitated a different procedure from that used in former work done in this laboratory. The tubes were gently heated at the tip to drive from the tip any adherent liquid. They were then scored with a file and the tips broken off. The contents of the tube were then transferred to a flask by a capillary pipet, and the tube and pipet washed out four times thoroughly with alcohol that had been distilled from caustic potash. The contents of the flask were then diluted to 25 cc. with the same alcohol. The acid remaining was then titrated, using phenolphthalein as indicator. An alcohol correction of 0.05 cc. was deducted to correct for the apparent acidity as determined for the amount of alcohol present.

Experimental.

In this investigation the points of interest were the limits of esterification and the effect of varying concentration of the reagents on the limits.

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The letters used in tabulating results are those usually found in text-book expressions of the mass law.

A — Weight of alcohol or water in grams.
B — Weight of acid or ester in grams.
p — Active mass of alcohol or water in millimoles.
q — Active mass of acid or ester in millimoles.
alk. — Cc. of standard alkali required in titration.
x — Millimoles of reagents transformed when equilibrium is reached, which is equivalent to the amount of ester and water formed in the acid series, and the alcohol and acid formed in the ester series.
$p - x$ — Millimoles alcohol remaining (acid series) millimoles water remaining (ester series).
$q - x$ — Millimoles acid remaining (acid series) millimoles ester remaining (ester series).
r — The equilibrium constant.
% — Per cent. esterification calculated for formula given below.

In the acid series at equilibrium we get from the titration the concentration of acid remaining $q - x$, from which by subtraction we get x, the concentration of the ester and water formed, and from this value that of the alcohol remaining $p - x$. The equilibrium constant is then obtained.

$$\frac{[\text{Water}] \times [\text{Ester}]}{[\text{Alcohol}] \times [\text{Acid}]} = \frac{x^2}{(p - x)(q - x)} = r.$$

In the ester series at equilibrium, we get from the titration the concentration of acid and alcohol formed, x, which also, by subtraction from the original concentrations of water and ester, gives the concentrations of these untransformed. From these data we obtain our equilibrium constant

$$\frac{[\text{Water}] \times [\text{Ester}]}{[\text{Alcohol}] \times [\text{Acid}]} = \frac{(p - x)\,(q - x)}{x^2} = r.$$

To calculate the percentage of equivalent amounts esterified at equilibrium we use the formula given by Reid,[1] and more fully explained by Faber and Reid,[2]

$$\% = \frac{100}{\sqrt{r} + 1}.$$

The heating was continued either 96 or 192 hours, as it was found with methyl and ethyl alcohol and benzoic acid that after 48 hours' heating the percentages esterified at the limit in the acid series were about 2 or 3% less than in the ester series.

[1] *Am. Chem. J.*, 43, 499 (1910).
[2] THIS JOURNAL, 39, 1930 (1917).

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Experimental Results.

Series I.—96 Hours at 200°.

$CH_3OH + C_6H_5COOH$.

Expt. No.	1.	2.	3.	4.	5.
p	2.885	3.621	4.936	7.826	7.158
q	4.787	3.844	2.923	4.168	3.735
p/q	0.60	0.94	1.69	1.83	1.92
x	2.426	2.602	2.464	3.620	3.620
$p - x$	0.4584	1.019	2.471	4.206	4.206
$q - x$	2.361	1.242	0.4585	0.5484	0.5484
r	2.332	2.312	2.315	2.383	2.332
%	69.99	69.80	69.84	70.44	69.99
				Mean,	70.02%

$H_2O + C_6H_5COOCH_3$.

Expt. No.	6.	7.	8.	9.	10.
p	1.871	2.194	2.731	4.918	5.528
q	4.962	4.402	4.013	4.895	4.475
p/q	0.38	0.50	0.68	1.00	1.24
x	0.7694	0.9014	0.9693	1.477	1.502
$p - x$	1.101	1.203	1.762	3.441	4.026
$q - x$	3.293	3.501	3.044	3.418	2.973
r	2.475	2.276	2.389	2.321	2.304
%	70.55	69.48	70.49	69.89	69.73
				Mean,	70.03%

$C_2H_5OH + C_6H_5COOH$.

Expt. No.	11.	12.	13.	14.	15.
p	2.645	3.238	4.223	4.295	4.178
q	4.194	3.274	4.096	3.353	2.734
p/q	0.63	0.99	1.03	1.28	1.53
x	2.105	2.162	2.760	2.468	2.134
$p - x$	0.5397	1.076	1.463	1.828	2.045
$q - x$	2.089	1.112	1.336	0.8849	0.6006
r	1.983	1.976	1.974	1.941	1.925
%	66.48	66.40	66.38	65.99	65.82

Expt. No.	16.	17.	18.	19.	20.
p	2.986	3.755	4.023	4.013	3.968
q	5.125	3.121	3.286	3.249	3.014
p/q	0.58	1.20	1.22	1.23	1.32
x	2.431	2.244	2.381	2.358	2.239
$p - x$	0.5551	1.511	1.642	1.655	1.729
$q - x$	2.694	0.8772	0.9045	0.8918	0.7755
r	1.988	1.949	1.954	1.940	1.934
%	66.53	66.09	66.15	65.99	65.91
				Mean,	66.17%

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SERIES I (*continued*).

$H_2O + C_6H_5COOC_2H_5$.

Expt. No.	21.	22.	23.	24.	25.
p	2.673	5.198	11.101	10.702	10.996
q	3.231	4.181	6.465	4.769	4.667
p/q	0.83	1.24	1.72	2.25	2.36
x	0.988	1.576	2.828	2.332	2.306
$p - x$	1.684	3.622	8.273	8.369	8.690
$q - x$	2.242	2.604	3.638	2.436	2.361
r	1.966	1.948	1.940	1.936	1.965
%	66.28	66.08	65.99	65.94	66.27

Expt. No.	26.	27.	28.	29.	30
p	2.956	2.850	3.114	3.372	3.708
q	2.048	2.898	2.948	2.861	3.161
p/q	0.97	0.98	1.06	1.18	1.18
x	1.010	0.970	1.025	1.049	1.154
$p - x$	1.946	1.880	2.089	2.323	2.554
$q - x$	2.038	1.928	1.923	1.812	2.007
r	1.972	1.963	1.955	1.956	1.961
%	66.35	66.25	66.16	66.17	66.23
				Mean,	66.17%

$C_3H_7OH + C_6H_5COOH$.

Expt. No.	31.	32.	33.	34.	35.
p	2.171	3.390	2.963	3.545	5.063
q	4.737	3.830	2.933	3.289	3.006
p/q	0.46	0.89	1.01	1.08	1.69
x	1.867	2.399	1.972	2.276	2.423
$p - x$	0.3037	0.9906	0.9912	1.269	2.640
$q - x$	2.870	1.430	0.9610	1.013	0.5832
r	2.000	2.015	2.021	2.007	1.953
%	65.89*	66.84	66.90	66.74	66.13*

Expt. No.	36.	37.	38	39.	40.
p	3.424	3.515	2.946	3.160	4.557
q	3.725	3.386	2.780	2.793	3.916
p/q	0.92	1.04	1.06	1.13	1.16
x	2.384	2.303	1.909	1.973	2.800
$p - x$	1.040	1.212	1.037	1.187	1.757
$q - x$	1.341	1.083	0.870	0.820	1.116
r	2.018	2.026	2.010	2.004	1.999
%	66.87	66.95	66.78	66.71	66.58
				Mean,	66.80%

* Not used in taking average.

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SERIES II.—192 HOURS AT 200°.

$CH_3OH + o\text{-}CH_3C_6H_4COOH$.

Expt. No.	41.	42.	43.
p	6.818	7.008	7.992
q	3.028	2.846	2.671
p/q	2.25	2.46	2.99
x	2.636	2.514	2.386
$p - x$	4.182	4.695	5.606
$q - x$	0.3915	0.3321	0.2853
r	2.061	2.013	1.886
%	67.33	66.81	65.36[a]
		Mean,	67.06%

$C_2H_5OH + o\text{-}CH_3C_6H_4COOH$.

Expt. No.	44.	45.	46.	47.	48.
p	3.543	3.262	3.865	4.643	5.143
q	2.773	2.495	2.788	2.086	2.015
p/q	1.28	1.31	1.39	2.22	2.57
x	2.055	1.862	2.094	1.773	1.748
$p - x$	1.488	1.399	1.771	2.870	3.395
$q - x$	0.718	0.6327	0.6933	0.3132	0.2664
r	1.988	1.979	1.890	1.870	1.839
%	66.53	66.44	65.40	65.16	64.77
				Mean,	65.66%

$C_3H_7OH + o\text{-}CH_3C_6H_4COOH$.

Expt. No.	49.	50.	51.	52.	53.
p	2.919	3.654	3.325	3.537	4.464
q	2.985	2.775	2.207	2.162	2.731
p/q	0.98	1.32	1.51	1.64	1.64
x	1.977	2.097	1.743	1.745	2.201
$p - x$	0.9420	1.556	1.582	1.792	2.263
$q - x$	1.008	0.6777	0.4644	0.4167	0.5301
r	2.029	2.042	2.034	2.020	2.010
%	66.99	67.13	67.04	66.89	66.77
				Mean,	66.96%

SERIES III.—192 HOURS AT 200°.

$CH_3OH + m\text{-}CH_3C_6H_4COOH$.

Expt. No.	54.	55.	56.	57.	58.
p	4.970	3.940	5.242	4.692	4.911
q	3.499	2.710	3.249	2.701	2.460
p/q	1.42	1.45	1.61	1.74	2.00
x	2.742	2.131	2.630	2.251	2.101
$p - x$	2.228	1.809	2.619	2.441	2.810
$q - x$	0.7569	0.5796	0.6192	0.4500	0.3591
r	2.112	2.081	2.065	2.147	2.091
%	67.86	67.54	67.37	68.23[a]	67.65
				Mean,	67.61%

[a] Not included in average.

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SERIES III (*continued*).

$C_2H_5OH + m\text{-}CH_3C_6H_4COOH$.

Expt. No.	59.	60.	61.	62.	63.
p	2.849	3.172	3.344	3.203	3.743
q	2.615	2.846	2.649	2.314	2.474
p/q	1.09	1.11	1.26	1.38	1.51
x	1.796	1.973	1.925	1.742	1.909
$p - x$	1.053	1.199	1.419	1.461	1.834
$q - x$	0.819	0.873	0.724	0.5715	0.5652
r	1.934	1.929	1.898	1.907	1.875
%	65.91	65.86	65.50	65.60	65.22
				Mean,	65.61%

$C_3H_7OH + m\text{-}CH_3C_6H_4COOH$.

Expt. No.	64.	65.	66.	67.	68.
p	2.430	3.028	3.489	3.545	3.686
q	3.084	2.932	3.101	2.668	2.588
p/q	0.78	1.03	1.12	1.33	1.42
x	1.792	1.984	2.177	2.000	1.985
$p - x$	0.637	1.044	1.311	1.544	1.701
$q - x$	1.291	0.948	0.923	0.668	0.603
r	1.975	1.994	1.978	1.970	1.960
%	66.39	66.30	66.43	66.33	66.21
				Mean,	66.39%

SERIES IV.—192 HOURS AT 200°.

$CH_3OH + p\text{-}CH_3C_6H_4COOH$.

Expt. No.	69.	70.	71.	72.	73.
p	3.787	4.238	4.987	5.004	5.391
q	3.204	2.520	2.793	2.133	2.232
p/q	1.18	1.68	1.79	2.34	2.42
x	2.359	2.056	2.340	1.859	1.963
$p - x$	1.427	2.182	2.648	3.146	3.428
$q - x$	0.844	0.4644	0.4536	0.2745	0.2682
r	2.149	2.043	2.135	2.000	2.043
%	68.25	67.13	68.10	66.67	67.14
				Mean,	67.46%

$C_2H_5OH + p\text{-}CH_3C_6H_4COOH$.

Expt. No.	74.	75.	76.	77.	78.
p	3.974	2.986	3.427	3.644	4.693
q	3.136	2.085	2.195	2.243	2.536
p/q	1.27	1.43	1.56	1.62	1.85
x	2.275	1.590	1.711	1.766	2.063
$p - x$	1.699	1.396	1.710	1.878	2.630
$q - x$	0.8613	0.4949	0.4842	0.4770	0.4734
r	1.882	1.913	1.877	1.866	1.849
%	65.30	65.67	65.24	65.11	64.90
				Mean,	65.24%

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SERIES IV (*continued*).

$C_3H_7OH + p\text{-}CH_3C_6H_4COOH$.

Expt. No.	79.	80.	81.	82.
p	2.569	2.889	2.953	3.921
q	2.579	2.685	2.255	2.427
p/q	1.00	1.08	1.31	1.61
x	1.709	1.841	1.679	1.927
$p - x$	0.859	1.047	1.275	1.825
$q - x$	0.869	0.843	0.5760	0.5004
r	1.978	1.960	1.959	2.017
%	66.42	66.21	66.21	66.85[a]
				Mean, 66.28%

SUMMARY OF RESULTS.

Percentage Esterified at Equilibrium.

Alcohol.	Methyl.	Ethyl.	Propyl.
Benzoic acid	70.02	66.17	66.80
o-Toluic acid	67.06	65.66	66.96
m-Toluic acid	67.61	65.62	66.39
p-Toluic acid	67.46	65.24	66.28

Discussion.

The foregoing results furnish fairly concordant values for the equilibria of the various acids with corresponding alcohols. Since the experimental error is greater the further the ratio of alcohol to acid is from unity, to obtain the most reliable values for the limit only those experiments have ben considered in which the ratio of alcohol to acid was less than 1.5. The limits are tabulated below and are slightly different from the averages given above.

Alcohol.	Methyl.	Ethyl.	Propyl.
Benzoic acid	69.98	66.22	66.80
o-Toluic acid	67.07	66.12	66.72
m-Toluic acid	67.70	65.62	66.39
p-Toluic acid	68.17	65.36	66.28

For the purpose of showing the effect of varying ratio of alcohol to acid as influencing the equilibrium, the results have been arranged in the order of increasing proportions of alcohol.

BENZOIC ACID.

Methyl alcohol.		Ethyl alcohol.		Propyl alcohol.	
Ratio.	Limit.	Ratio.	Limit.	Ratio.	Limit.
..	...	0.58	66.53	0.46	65.89
..	...	0.63	66.48	0.88	66.84
0.62	69.99	0.99	66.40	0.92	66.87
0.94	69.80	1.03	66.38	1.01	66.90
1.69	69.84	1.20	66.09	1.04	66.95
1.88	70.44	1.22	66.15	1.06	66.78
1.92	69.99	1.23	65.99	1.08	66.74
..	...	1.28	65.99	1.13	66.71
..	...	1.32	65.91	1.16	66.58
..	...	1.53	65.82	1.67	66.13

[a] Not included in average.

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This effect was studied particularly with ethyl alcohol.

ETHYL ALCOHOL.

o-Toluic acid.		m-Toluic acid.		p-Toluic acid.	
Ratio.	Limit.	Ratio.	Limit.	Ratio.	Limit.
1.28	66.53	1.09	65.91	1.27	65.30
1.31	66.44	1.11	65.86	1.43	65.67
1.39	65.40	1.26	65.50	1.56	65.24
2.23	65.16	1.38	65.60	1.62	65.11
2.55	64.77	1.52	65.22	1.85	64.90

From the tables above it appears that there is a gradual drop in the limit with increase of the ratio of alcohol to acid. The drop is slight and not much beyond the unavoidable experimental error, but as the trend in nearly all cases is in the same direction, it seems to be real.

The results of Berthelot and St. Gilles[1] have been recalculated for comparison and are given below, the first two columns being their figures, the last two being their figures recalculated to our basis.

	Ratio.	% esterification.	r.	Limit.
Methyl alcohol and benzoic acid	1.0	64.8	1.841	64.80
	3.0	87.4	1.689	62.81
Ethyl alcohol and benzoic acid	1.0	66.5	1.985	66.50
	2.0	83.1	1.870	66.15
	3.0	87.0	1.653	62.31
	4.0	89.3	1.549	60.77
Methyl alcohol and acetic acid	0.20	19.3	2.568	71.97
	0.45	39.0	2.287	69.58
	0.50	42.9	2.131	68.06
	0.67	54.6	2.301	69.71
	1.00	66.5	1.985	66.50
Ethyl alcohol and acetic acid	1.00	67.5	2.077	67.50
	1.50	75.9	1.796	64.24
	2.00	84.0	1.951	66.10

It appears from the results that the change of the limit of esterification is in the same general direction, although some of the individual determinations are out of line.

From the above it appears that for esterification, the mass law holds very nearly but not quite exactly. The gas law holds for perfect gases only, and correction terms must be inserted on account of the mutual attraction of the particles and also because the particles are not infinitely small. The mass law in its simplest form tacitly assumes that the four substances A, B, C and D have no influence whatever on each other except that the reaction $A + B \rightleftarrows C + D$ takes place. This assumption, though nearly correct, in some cases, can never be absolutely so. Sup-

[1] *Ann. chim. phys.*, [3] **68**, 275–279 (1862).

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pose, for instance, that A and C are very soluble in each other, more so than the other pairs; that is to say, that A and C have an attraction for each other, which we may call physical, but it would have the effect of restraining the molecules of these two substances, so to speak, from taking part in the reactions as they otherwise would, and hence diminish their effective concentrations. While the mass law probably holds absolutely in ideal cases, in actual cases we expect only approximations such as we find with the gas law when actual cases are considered.

The effect of isomerism, in the acids, on the limit found with mercaptans and the three toluic acids was worked out by Sachs and Reid.[1] These authors found that the limit with ethyl mercaptan was practically the same with the *o*-, *m*-, and *p*-toluic acids. The results obtained above with alcohols, however, show a variation in the limit. With methyl alcohol the limit rises from ortho, meta to para, while with ethyl and propyl alcohols the reverse is true. This exceptional behavior of methyl is also observed in the high value of the limit with benzoic acid.

Conclusions.

1. Esterification limits have been found for benzoic and the three toluic acids with methyl, ethyl and propyl alcohols.

2. The limits found vary only slightly with change of ratio of active masses, that is, the mass law holds very nearly.

3. With the exception of methyl alcohol the esterification limit rises with increase of molecular weight of the alcohol.

4. With methyl alcohol and the toluic acids, toluic acid shows the highest limit, *o*-toluic acid the lowest.

5. The reverse is true of ethyl and propyl alcohols and the toluic acids.

6. These acids have been found to be esterified very slowly by alcohols even at 200°, four days being required to reach the limit.

BALTIMORE, MD.

NEW BOOK.

Charles Anthony Goessmann. Published Jointly by the Corporation and the Associate Alumni of the Massachusetts Agricultural College; printed at the University Press, Cambridge, Mass., 1917.

A beautifully printed brochure from the Riverside Press at Cambridge, lies open before me. I see the impressive frontispiece—the portrait of Goessmann, in his prime. I look at the dignified features of one of the Big Four of the early Agricultural Chemists of the country, Johnson, Storer, Hilgard, Goessmann! Who of their successors will do more for agricultural science than they have done? Goessmann had a precious opportunity to prepare hinself for brilliant work and he embraced it to the fullest extent. He was first a pupil of and for five years assistant to

[1] THIS JOURNAL, 38, 2746 (1916).

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Wöhler. He was born at Naumburg, on the 13th of June, 1827, and died at Amherst, September 1, 1910, in his eighty-fourth year. In 1852 he became Doctor of Philosophy at Göttingen and was immediately made assistant to Wöhler. His earlier ambition was to be a pharmacist, and his doctor's dissertation was on "The Constituents of Cantharides." It was Wöhler who persuaded him to devote his life to chemistry. During the five years he was assistant to Wöhler his reputation as an investigator was firmly established. His early connection with agriculture is also noted at this time in the discovery of arachic acid in the peanut. He also, in collaboration with the late Professor Caldwell, discovered hypogaeic acid. His studies of leucin at this time led to the description of the first known amino acid. As a teacher at Göttingen he had among his pupils many Americans, who subsequently became ornaments to the profession, among them—Caldwell, Chandler, Clark, Garrigues, Hungerford, Joy, Mallet, Marsh, Nason, Pugh and Weyman.

Dr. Goessmann gave up his career at Göttingen to enter the field of applied chemistry. He came to America by invitation of the Eastwick Brothers, of Philadelphia, to improve the processes for the refining of sugar. During his whole career he took the deepest interest in all problems relating to that industry. Wöhler was much disturned at his departure and wrote to Liebig: "Unfortunately I am to lose him, for five years my assistant and known to you through his works." Could any greater compliment have been paid to a young chemist than being regretted by Wöhler?

During his service with the Eastwicks, Goessmann made the first extensive chemical studies of sorghum, as a sugar-producing plant, and it was through these studies that the writer first became acquainted with him. The results of these studies were submitted to Wöhler and were published, after his endorsement, in the *Journal für Landwirthschaft.*

It was just at this time (1858) that a few seeds of sorghum were sent by our Congressman to my father, who turned them over to me. I planted them and in the autumn, expressing a small quantity of juice by torsion, made my first experiment in the manufacture of sorghum sirup.

From the refining of sugar Goessmann was called to another important agricultural problem, *viz.*, making salt for butter. As long as a deranged taste leads us to prefer a salty butter, it is well to have the pure salt.

While at Syracuse he was appointed professor at the Rensselaer Institute, at Troy, at the request of Professor Chandler and served there for two years.

During the Civil War (why Civil?) Goessmann was proposed by Wöhler for the professorship of Chemistry in the Braunschweig Technical High School. He wrote to Wöhler that the political affairs of this country were so mixed that little hope for the future was promised. He, therefore,

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was greatly pleased at the prospect of returning to so promising a post in his fatherland. For some reason this plan, fortunately for this country, was never carried out and Goessmann was saved for his great work at the Massachusetts Agricultural College.

He accepted this post on May 16, 1868. At this time he was forty-one and is described by President Clark as a "hearty, full-blooded, wide-awake, nervous German. I will not compare him to Agassiz, but I will say that he is a man of temperament something like his." At the same time Agassiz wrote: "I know of his work as a scientific chemist and I do not believe you could have had a better appointment. It is not a very dangerous thing to take professors from foreign parts. I am such an one and have in a measure succeeded in making myself a native American." So did Goessmann. So have done, thank God, so many of our foreign-born citizens. At Amherst, Goessmann continued his studies with sugar-producing plants, but this time with a more promising subject than sorghum, *viz.*, the sugar beet. With seeds obtained from Germany, he continued the experimental work with sugar beets, begun in this country in 1835 and spasmodically continued to 1884. He contributed freely to *The American Chemist*, founded by Professor Chandler, in 1870.

Becoming a member of the State Board of Agriculture, in 1873, he published a paper on commercial fertilizer which had for its *leit motif* the slogan —"to state what they sell and sell what they state." This secured the passage, by the State of Massachusetts, of the first fertilizer control act in this country.

His work in agriculture from that time to his death is an integral part of scientific agriculture in all the states. Notable particularly are the establishment of the silo, the promotion of the sugar industry, the chemistry of fruits, scientific feeding experiments, and the economical use of fertilizers.

Of particular interest to agricultural chemists is the fact that Goessmann was the Maecenas, *pater carissimus*, of the Association of Official Agricultural Chemists. At a meeting of agricultural chemists held in Washington in 1880, he offered the following resolution:

"*Resolved*, That this Convention form a section in the sub-division of Chemistry of the American Association for the Advancement of Science, and that the next meeting be held in Boston, during the regular meeting of the aforesaid Association."

Although no stable organization resulted from this effort, it at least bore fruit in the organization of the Association in Philadelphia four years later. Since that date the Association has grown steadily in number and influence and now has nearly 300 members. Through its work the science of agricultural chemistry has been placed on a plane in this country higher than in any other country of the world.

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Of particular interest to chemists are selections from the correspondence with Wöhler which are given in the last pages of the Memorial. In a letter to Goessmann, dated March 12, 1860, Wöhler announces the discovery of cocaine in the following modest words:

"At present I am having Niemann make an investigation of the famous Coca (*Erythroxylon coca* of Peru) and, as far as we have ascertained, it very probably contains an organic base which may be crystallized and which resembles atropin. We have christened it Cocaine."

Again, under date of August 1, 1866, Wöhler wrote:

"Last month when the king with the whole Hanoverian army and all the munitions of war took refuge here, we were living in a wild, great military camp, daily fearing the outbreak of a battle in our immediate neighborhood. After the departure of our army Göttingen was occupied by the Prussians. Then came the disastrous battle of Langensalza, followed by the capitulation of our army. The Prussians have also been victorious in the south, where they occupy all of Hesse, Nassau, Darmstadt, Frankfurt and a great part of Bavaria. Their troops are already near or in Würzburg. At present there is an armistice. It is said that all of Hanover, the Electorate of Hesse, and Nassau will be annexed to Prussia. But enough of these painful events."

And on December 17, 1868:

"Here everything is going its old course, with some modifications, since we are Prussians."

How pathetic! Dear old Wöhler trying to be a good Prussian! First the rape of Schleswig-Holstein, and then, alas, poor Hanover! Soon the intoxication of Sedan was to come, the stain of which victorious Verdun has washed away.

As a teacher, Goessmann was greatly beloved by his pupils. He was not only their instructor, but their friend and mentor. He had brought with him not only the spirit but the method of his own master at Göttingen. Every one of his pupils was a grandson of Wöhler. Goessmann was a deeply religious man. Born and brought up in the Catholic church, he remained a devout member thereof to the end of his days. He was as reverent in the presence of a fact as Faraday. He was methodic in all his activities and devoid of undue haste to a truly German degree. While one could always detect that he was a foreigner by his speech, he had complete mastery of the English language with his pen, and was a prolific writer on scientific subjects. The titles of 362 papers are given in the Memorial. He loved the quiet and academic repose of his beautiful home at Amherst and in his later days he never even attended the meetings of the Association of Official Agricultural Chemists, of which he was the founder. His first chemical paper was published in 1853, being his dissertation on the components of the Spanish fly. His last

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publication was issued in 1907, entitled "Instructions Regarding the Sampling of Materials to be Forwarded for Analysis."

Had Goessmann continued his research work he perhaps might have attained a higher rank among the chemists of the world, but he would not have performed the service to science and to humanity which he did. We are deeply indebted to Frederick Tuckerman, Joseph B. Lindsey and Charles Wellington, the Committee, entrusted with the preparation of the Memorial which they very appropriately prefaced by a translation from the inscription on Fichte's monument in Berlin:

"Teachers shall shine
As the brightness of the Firmament;
And they that lead many to truth
As the stars for ever and ever."

HARVEY W. WILEY.

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[COMMUNICATION NO. 59 FROM THE RESEARCH LABORATORY OF THE EASTMAN KODAK COMPANY.]

THE IODIDE TITRATION OF SILVER NITRATE WITH PALLADIOUS NITRATE AS THE INDICATOR.[1]

BY LOUIS SCHNEIDER.

Received October 17, 1917.

Introduction.

Of the rapid volumetric methods used for the silver titrations, the Volhard method is the most widely employed. The limitations of this method are many, as summarized by Dewey,[2] who makes the following statement:

"When the Volhard method is applied to miscellaneous materials some objections appear. Mercury and palladium interfere. No objection is made to moderate amounts of copper and platinum. It is often said that 70% Cu may be present, but this is certainly a mistake. Nickel and cobalt obscure the end color. It has been suggested when Ni and Co are present to add excess of sulfocyanate and titrate back with silver. Chloride of silver must be absent since it gradually reacts with sulfocyanate in solution. Lower oxides of nitrogen must be absent. Ferrous iron, in presence of nitric acid, must not be used as the indicator since this would mean lower oxides of nitrogen. It should be noticed that ferric sulfate as an indicator may cause precipitation of lead sulfate when the bullion contains lead."

Further,

"for those cases in which the amount of silver is extremely small or the solution highly

[1] A paper read before the American Chemical Society, at the Boston meeting, September, 1917.

[2] F. P. Dewey, *J. Ind. Eng. Chem.*, 6, 728 (1914).

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dilute, it (the Volhard method) lacks the sensitiveness of the methods of Gay Lussac or Pisani."[1]

The palladium method is especially adapted for the determination of very small amounts of silver with a satisfactory accuracy and overcomes the effect of those metals that usually interfere with the Volhard method. This new method consists of the titration of silver nitrate with potassium iodide in the presence of a very small amount of palladious nitrate. The silver nitrate is precipitated by the potassium iodide and the slightest excess of potassium iodide is converted by the palladious nitrate to palladious iodide.

Standard Solutions.

The solutions required for the palladium method were very easily and rapidly prepared. The standard silver solution of tenth-normal strength was prepared by weighing fused silver nitrate[2] previously ground, heated to 160° for one-half hour and cooled in a desiccator. The hundredth- and the thousandth-normal silver solutions were prepared by the proper and careful dilution of this tenth-normal solution.

For this investigation, the potassium iodide (Kahlbaum) was ground and heated at 160° for one hour, then accurately weighed to make a tenth-normal solution. The hundredth- and the thousandth-normal solutions were prepared by the dilution of the tenth-normal solution. For ordinary practice it would not be necessary to exercise such care to prepare an approximately tenth-normal potassium iodide solution. However, if C. P. potassium iodide is properly dried and carefully weighed to make a tenth-normal solution, the potassium iodide solution would need no further standardization by silver nitrate, provided the recommended conditions for titration are followed and the constant error correction of 0.03 cc. applied when 0.1 *N* potassium iodide solution is employed. This latter procedure does not necessitate, for determinations of ordinary accuracy, the preparation of a standard silver nitrate solution.

Indicator.

The palladious nitrate indicator used in this investigation was a solution of palladious nitrate in 16% nitric acid (free from nitrous acid) with a metal content of 0.06%. The palladious nitrate solution may be prepared by dissolving the weighed palladium in nitric acid and evaporating to dryness, then dissolving the crystals in 15 to 20% nitric acid (free from nitrous acid) and filtering.

In applying the palladium indicator it was found advisable to employ

[1] L. W. Andrews, *Am. Chem. J.*, **24**, 256 (1900).

[2] The silver nitrate used was that prepared by the Eastman Kodak Company and conformed to the requirements of acidity and permanganate number as specified for the silver voltameter. Rosa, Vinal and McDaniel, "The Silver Voltameter," *Bull. Bur. Stand.*, **9**, 526.

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a protective colloid to prevent the occlusion of silver nitrate or potassium iodide in tenth-normal titrations. Then, again, for very dilute solutions, the use of a protective colloid was necessary in order to obtain a precise colorimetric comparison in determining the end point. It was found most advantageous to use an addition of a 5% gum arabic solution to the silver nitrate solution to be titrated. This addition of gum arabic afforded very good precision and satisfactory accuracy.

Other protective colloids were tried, such as soluble starch, gelatine, agar-agar, gum tragacanth and white dextrine. The order of their usefulness as protective colloids is, respectively, (1) gum arabic, (2) gelatine and agar-agar, (3) gum tragacanth, (4) dextrine, and (5) soluble starch.

For tenth-normal concentrations of silver nitrate, 5 cc. of a 5% gum arabic solution were used, whereas for thousandth-normal solutions, 1 cc. was sufficient because of the dilution of the electrolytes. To prevent decomposition of the gum arabic solution, a small amount of thymol (less than 0.1 g. per 100 cc. of solution) was added to the filtered gum arabic solution which then kept for months without any signs of decomposition or mould growth.

Containers.

The titration may be made in various containers such as porcelain crucibles, casseroles, evaporating dishes or in square bottles.[1] Although fairly good precision can be obtained with porcelain ware, the square wide-mouthed bottles of colorless glass are preferred and recommended. When these bottles are placed on an evenly illuminated sheet of opal glass or white paper, they enable one to make a precise comparison, whenever necessary, of the colors of the supernatant liquids by transmitted light viewed against a white background. Three sizes of the square bottles were employed; the smallest had a diameter of 46 mm. and 60 cc. capacity, another a diameter of 55 mm. and 130 cc. capacity, and the largest a diameter of 70 mm. and 250 cc. capacity.

Sensitiveness of Indicator.

The visibility of palladious iodide, as determined by adding 0.2 cc. of 0.0002 *N* potassium iodide to 10 cc. water containing 0.25 cc. palladious nitrate indicator, was 1 part in 1,400,000 parts of solution.[2] The coloration of the liquid was reddish brown and easily discernable, comparison with a blank being unnecessary. Of course, under these conditions, the optimum sensibility was reached since no silver iodide was present to interfere with the coloration of the liquid. However, under working conditions as for example the titration of silver nitrate with tenth-normal potassium

[1] W. M. Dehn, This Journal, 39, 1392 (1917).

[2] R. Kersting, *Ann.*, 87, 19 (1853), in the estimation of potassium iodide with palladious chloride, obtained a faint brown coloration with an iodine content of 1 part in 1,000,000.

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iodide, a sensibility of 1 part in 500,000 parts of solution was obtained without any difficulty.

Series of experiments were made to determine (1) the minimum amount of indicator required to produce a definite end point for various concentrations of silver nitrate with and without gum arabic present, (2) the influence of the dilution of tenth-normal silver nitrate solutions upon the sensitiveness of a fixed quantity of the indicator, and (3) the influence of various concentrations of palladium upon a fixed concentration of silver.

I. Effect of Dilution on Sensitiveness of Indicator.

A series of experiments similar to that given in Table I was conducted with the use of 1 cc. 0.1 *N* silver nitrate instead of 5 cc. The results were practically the same since only 0.03 to 0.04 cc. of 0.1 *N* potassium iodide was required to produce the brown coloration at the end point. The color of the end point obtained in Expt. 5 was reddish brown, which was considerably less intense than the color in the other experiments, and proved to be at the limit of easy discernability of the end point, without the use of a blank or comparison standard. Therefore, it may be concluded from the

TABLE I.—EFFECT OF DILUTION ON SENSITIVENESS OF INDICATOR.

NOTE.—In each of the following experiments, 0.5 cc. of the palladious nitrate indicator and 5 cc. of a 5% gum arabic solution were used:

Expt.	Cc. water added.	Cc. 0.1 *N* $AgNO_3$.	Cc. 0.1 *N* KI.
1	0	5.00	5.02[1]
2	25	5.00	5.02
3	50	5.00	5.05
4	100	5.00	5.05
5	200	5.00	5.03

experiments in Table I, that dilutions of 0 to 200 cc. of water are without any appreciable influence upon the determination of the end point under the specified conditions.

II. Influence of Concentration of Palladious Nitrate.

The series of experiments in Table II shows that the concentration of the palladium is without any influence upon the determination of the silver content. With 0.25, 0.5 and 1 cc. of the palladious nitrate indicator approximately eight minutes were consumed for the completion of the titration, but with 2 and 5 cc. of the indicator the time required was 24 and 32 minutes, respectively. This considerable increase of time was necessitated by the slow conversion of the large amount of palladious iodide, formed near the real end point, over to silver iodide. In Expts. 9 and 10, the values of 0.1 *N* potassium iodide marked "initial" were obtained at the

[1] The smallest divisions on the burets were 0.05 cc. The readings were estimated to 0.01 cc. The burets were certified and the corrections on the certificates were given to 0.01 cc.

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end of seven minutes, when a deep dark brown coloration first persisted throughout the whole liquid. Constant agitation caused the palladious iodide to be quickly converted over to silver iodide whereas the further addition of a drop of potassium iodide solution again caused a dark brown

TABLE II.—INFLUENCE OF CONCENTRATION OF PALLADIOUS NITRATE.

NOTE.—In each of the following experiments, 50 cc. of water and 5 cc. of a 5% gum arabic solution were used:

Expt.	Cc. indicator added.	Cc. 0.1 N $AgNO_3$.	Cc. 0.1 N KI required.	Time required for complete titration. Minutes.
6.....	0.25	5.00	5.03	8
7.....	0.5	5.00	5.05	6
8.....	1.0	5.00	5.03	7
9.....	2.0	5.00	4.97 Initial 5.04 Final	24
10.....	5.0	5.00	4.78 Initial 5.02 Final	32

coloration of the liquid. This procedure of slow addition and constant stirring finally gave a coloration which persisted at the end of 5 minutes' agitation. In all cases where the color remained after 5 minutes' agitation, the end point proved to be the real and not the apparent one because the coloration persisted even overnight and was permanent.

III. The Optimum Quantity of Indicator for Various Dilutions.

The volumes of indicator that were used in this series of experiments were 0.25, 0.5 and 1 cc., since with these volumes the true end point was obtained within a reasonable length of time (see Table II). From the several experiments that were carried out, the following conclusions were drawn:

(1) For titrations of 0.1 N silver nitrate with 0.1 N potassium iodide in the presence of gum arabic, either 0.5 or 1 cc. of the indicator may be used with equally good effect for total volumes up to 125 cc. For volumes from 125 to 225 cc., the amount of indicator necessary for the easy determination of the end point is 1 cc.

(2) For titration of 0.1 N silver nitrate with 0.1 N potassium iodide without gum arabic, at least 1 cc. of the indicator is required for all volumes ranging up to 225 cc.

Permanency of End Point.

The permanency of the end point as obtained with palladious nitrate is very satisfactory. This is due to the stability of palladious iodide, and its inappreciable absorption to silver iodide. It is well known that the color (ferric sulfocyanate) obtained at the end point in a Volhard titration gradually fades in the presence of silver sulfocyanate, especially at high temperatures. On the other hand, with the palladious iodide end point neither temperature nor long standing affects its stability. For instance, when a check titration of thousandth-normal silver nitrate with thousandth-

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normal potassium iodide was carried out in the presence of gum arabic, the brown color of the suspended palladious iodide persisted for over a week without any appreciable change in the intensity of the color.

Limits of Accuracy of the Method.

The reproducibility is fair when titrations are carried on in porcelain ware but a better precision is obtained with square bottles of clear glass. It has been found that especially with thousandth-normal solutions a very satisfactory precision can be obtained by the addition of a 5% solution of gum arabic to the solution to be titrated. The gum arabic prevents precipitation of the silver iodide and keeps the palladious iodide formed at the end of the reaction uniformly suspended throughout the liquid. It also prevents the formation of a scum of silver iodide on the surface of the liquid, as is the case when gum arabic is absent. This scum seriously interferes with the determination of the end point for thousandth-normal titrations when the intensity of the coloration of the liquid is observed from above. On account of this even distribution of the suspended palladious iodide, checks can be made easily and a single blank can be used for the day without fearing alteration of the intensity of the color. The intensity remains unaltered even for fairly high temperatures provided the concentration of the nitric acid is not too great. Other factors to be considered and observed are the sufficient dilution of tenth-normal silver nitrate solutions in the absence of gum arabic, the constant agitation of the liquid to be titrated and the slow addition of the titration solution.

Finally, for thousandth-normal titrations care was exercised in the selection of the intensity of the color to be employed for comparison. A fairly intense reddish brown coloration was selected for the comparison standard, usually 3.0 cc. of 0.001 potassium iodide developed this coloration. This amount corresponds to the 0.03 cc. of 0.1 potassium iodide which was necessary to produce a satisfactory coloration at the end point in tenth-normal titrations. The necessity for the selection of a good coloration for thousandth-normal solutions is due to the color effect of the silver iodide formed in the titration. If all these factors are considered there should be no difficulty in securing a very satisfactory precision under various conditions.

When the necessary precautions and conditions as previously stated are observed for titrations of silver solutions with tenth- or hundredth-normal potassium iodide solution, the uncorrected error ranges from 0.1% to 0.5%; whereas after a constant error correction of 0.03 cc. of 0.1 N or 0.01 N potassium iodide solution is applied, an accuracy of 0.1% is easily obtained. For thousandth-normal titrations, the error ranges from ±0 to 1.0%, which must be regarded as being satisfactory on account of the low silver content. In Expt. 17 (Table IV) the silver content was slightly more than 0.1 mg. and this amount was determined within 1%, which is

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very satisfactory for such a small amount of silver. In the presence of other metallic salts, the silver, which was titrated with 0.1 *N* potassium iodide solution, was determined with a corrected error of approximately 0.1%; for thousandth-normal titrations with colored metallic salts present, a silver content of a milligram was determined with an accuracy of 0.6% and less. The accuracy therefore for various concentrations of silver under various conditions seems, therefore, to be quite satisfactory.

TABLE III.—TITRATIONS WITH 0.1 *N* AND 0.01 *N* POTASSIUM IODIDE SOLUTIONS.

NOTE.—In these experiments, no blanks or comparison standards were employed. The constant error correction applied to 0.1 *N* titrations was 0.03 cc. of 0.1 *N* KI, likewise the correction was 0.03 cc. 0.01 KI for 0.01 *N* titrations when the end point was a faint reddish brown. A darker coloration caused by the further addition of a drop of 0.01 *N* KI would require a correction of 0.08 cc. 0.01 *N* KI.

Expt.	Cc. indicator.	Cc. water added.	Cc. 5% gum arabic solution.	Cc. $AgNO_3$. 0.1 *N*.	Cc. KI. 0.1 *N*.	G. Ag taken.	G. Ag found.	Error. %.	Corrected error. %.
11	0.25	50	5	5.00	5.03	0.0539	0.0542	+0.55	±0
12	0.5	25	5	20.00	20.05	0.2157	0.2162	+0.23	+0.1
13[1]	0.5	..	..	20.00	20.05	0.2157	0.2162	+0.23	+0.1
14	0.5	25	5	25.00	25.04	0.2697	0.2701	+0.14	+0.04
				0.01 *N*.	0.01 *N*.				
15	0.5	..	1	10.00	10.04	0.01078	0.01082	+0.37	+0.1
16	0.5	20	1	10.00	10.04	0.01078	0.01082	+0.37	+0.1

TABLE IV.—TITRATIONS WITH 0.001 *N* POTASSIUM IODIDE SOLUTION.

NOTE.—Five cc. of a 5% gum arabic solution were used in all of the following experiments. The "blank correction" was obtained by determining the number of cc. of 0.001 *N* KI solution required under similar conditions to produce a definite intensity of the coloration at the end point.

Expt.	Cc. indicator.	Cc. 0.001 *N* $AgNO_3$.	Cc. 0.001 *N* KI.	Blank correction. Cc. 0.001 *N* KI.	Mg. Ag taken.	Mg. Ag found.	Error. %.
17[2].....	0.25	1.00	3.26	2.27	0.107	0.106	—0.93
18.....	0.25	10.00	12.72	2.75	1.078	1.075	—0.27
19.....	0.25	10.00	12.75	2.75	1.078	1.078	±0
20.....	0.25	10.00	12.76	2.75	1.078	1.079	+0.09
21.....	0.25	20.00	22.77	2.75	2.156	2.159	+0.13
22.....	0.50	25.00	28.15	3.20	2.695	2.690	—0.18
23.....	0.50	25.00	28.16	3.20	2.695	2.691	—0.14
24.....	0.50	50.00	53.80	3.90	5.394	5.376	—0.33

Effect of Metallic Salts.

A few experiments were tried with the addition of a metallic salt in order to determine the effect of the colored metallic salts or of the metal itself. In all cases with the colored metallic nitrates, such as the nitrates of copper, nickel and cobalt, no difficulty was encountered in easily observing the end point. With the tenth-normal titrations, the end point was obtained

[1] Temperature = 72°.

[2] 15 cc. H_2O were added to the silver nitrate solution before titration.

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by observing the supernatant liquid by transmitted light against a white background until the black precipitate of the palladious iodide presisted after vigorous stirring for 5 minutes. The end point with the thousandth-normal solution in these particular experiments recorded was determined by comparison, by reflected light, of the upper surface of the liquid against a similar blank.

TABLE V.—EFFECT OF METALLIC SALTS (0.1 *N* TITRATION).

NOTE.—In the following experiments the metals were added as the nitrates. The end point was obtained without the use of a blank or comparison standard, except in the case of the mercury experiment. The percentages listed under the column headed "Corrected Error" were obtained by applying a constant error correction of 0.03 cc. 0.1 *N* KI.

Expt.	Cc. indicator.	Cc. substances added.	G. metal added.	Cc. 0.1 *N* $AgNO_3$.	Cc. 0.1 *N* KI.	G. Ag taken.	G. Ag found.	Error. %.	Corrected error. %.
25	0.5	45 H_2O	0.0655 Cu	10.00	10.05	0.1078	0.1083	+0.48	+0.15
26	0.5	45 H_2O	0.262 Cu	20.00	20.03	0.2157	0.2160	+0.13	±0
27	0.5	(45 H_2O + 5 cc. 5% G. A.)	0.262 Cu	20.00	20.03	0.2157	0.2160	+0.13	±0
28	0.5	45 H_2O	0.393 Cu	20.00	20.03	0.2157	0.2160	+0.13	±0
29	0.5	45 H_2O	0.065 Co	10.00	10.02	0.1078	0.1080	+0.15	—0.09
30	0.5	45 H_2O	0.260 Co	20.00	20.05	0.2157	0.2162	+0.23	+0.09
31	0.5	(45 H_2O + 5 cc. 5% G. A.)	0.260 Co	20.00	20.04	0.2157	0.2161	+0.18	+0.04
32	0.5	25 H_2O	0.096 Ni	10.00	10.05	0.1078	0.1083	+0.46	+0.15
33	0.5	45 H_2O	0.384 Ni	20.00	20.05	0.2157	0.2162	+0.23	+0.09
34	0.5	(45 H_2O + 5 cc. 5% G. A.)	0.384 Ni	20.00	20.08	0.2157	0.2166	+0.41	+0.23
35	0.5	50 H_2O	0.162 Hg	10.00	10.05	0.1078	0.1083	+0.46	+0.15
36	0.5	25 H_2O	0.117 Cd	10.00	10.04	0.1078	0.1082	+0.37	+0.09
37	1.0	30 H_2O	0.702 Cd	20.00	20.09[1]	0.2157	0.2167	+0.46	+0.27

TABLE VI.—EFFECT OF METALLIC SALTS (0.001 *N* TITRATION).

NOTE.—In the following experiments the metallic salts were added as the nitrates. The "blank correction" was obtained by running a parallel experiment and determining the number of cc. of 0.001 *N* KI that were necessary to produce the definite hue required.

Expt.	Cc. indicator.	Substances added.	Mg. metal added.	Cc. 0.001 *N* $AgNO_3$.	Cc. 0.001 *N* KI.	Blank correction. Cc. 0.01 *N* KI.	Mg. Ag taken.	Mg. Ag found.	Error. %.
38	0.25	10 cc. H_2O + 5 cc. 5% G. A.	13.1 Cu	10.00	13.46	3.40	1.078	1.085	+0.63
39	0.25	10 cc. H_2O + 5 cc. 5% G. A.	13.0 Co	10.00	13.24	3.20	1.078	1.083	+0.46

In the particular case of mercury nitrate, sufficient time (5–10 mins.) and constant agitation must be given for the yellow mercuric iodide formed at the end point to go into solution again in order to distinguish the coloration due to palladious iodide. This coloration increases with time until

[1] Coloration at end point grew darked upon long standing. G. A. = gum arabic.

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all the mercuric iodide is converted over to palladious iodide. The end point was obtained in this experiment by matching against a similar precipitation with indicator absent.

No attempt was made to determine the limit of the amount of each metal that may be present without interfering with the accuracy of the determination of the silver. Nevertheless the results show that the amount of metal or metals that may be present is a large percentage of the total metal content in the solution.

Errors.

There are present both the plus and minus errors, usually inherent in nearly all analytical work. The plus error, particularly for tenth-normal solutions, is the occlusion of potassium iodide[1] in the precipitated silver iodide. This occlusion consequently causes an increased addition of the tenth-normal potassium iodide solution in order to obtain a coloration of the liquid. The error can be overcome for the most part by good stirring of the liquid together with the slow addition of the titration liquid, also either by dilution or by the addition of a gum arabic solution. Another source of the plus error is nitrous acid present in the nitric acid. The nitrous acid readily liberates iodine from the palladious iodide formed at the end of the reaction. The free iodine after being partly dissolved by the precipitated silver iodide, colors the liquid a light yellowish brown tint which is not to be confused with deep reddish brown color of the palladious iodide. This nitrous acid can easily be removed by boiling the silver solution before titration.

On the other hand, the minus error is due to the occlusion of silver nitrate[2] in the precipitated silver iodide. There are several methods for correcting this source of error. Sufficient dilution of the silver nitrate solution will do this, also good stirring and the slow addition of the potassium iodide solution. The method that proved to be the most effective was the addition of a 5% gum arabic solution to the solution to be titrated. The specific effect of the gum arabic is the prevention of a curdy precipitate of silver iodide, which is caused by local concentration, thus entrapping the mother liquor containing silver nitrate. Unless these precautions are observed, balanced errors are likely to occur. This is due to the fact that in the titration of the more concentrated solutions the silver iodide first precipitated will occlude silver nitrate (minus error); whereas near the end of the titration, the precipitate will occlude potassium iodide (plus error). The effect of the gum arabic is really equivalent to a very rapid stirring of the silver nitrate solution with a very slow addition of the titrating liquid. Finally it was thought possible to overcome this occlusion of

[1] Lottermoser and Rother, *Z. phys. Chem.*, 62, 359–383 (1908).

[2] Kothner and Aeuer, *Ann.*, 337, 123 (1904); Baxter, *Pub. Carnegie Inst.*, 135, 107 (1910).

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silver nitrate by heating the liquid to be titrated to a fairly high temperature (75°). Although this heat treatment reduced the time required for the titration, it was not so good as the use of the gum arabic.

Recommended Conditions.

To obtain good precision and satisfactory accuracy, it is necessary to observe the following conditions: First of all the usual precautions that are customarily practiced with any titration that involves precipitation should be observed, especially in reference to the slow addition of the titrating liquor as well as the constant agitation of the liquid. The titration should be effected preferably in square bottles of clear, colorless glass. As to the temperature of the liquid, room temperature is recommended although considerably higher temperatures do not affect the results provided the concentration of the nitric acid is sufficiently diluted not to dissolve palladious iodide or decompose silver iodide. The conditions already stated apply equally as well for both tenth-normal and thousandth-normal titrations, but the further procedure of either of these titrations is quite different.

I. For titrations with *thousandth-normal* potassium iodide, in order to obtain the end point so that the uncertainty is minimized to the utmost, it is proposed that the titrations be carried on in the presence of a gum arabic to prevent the precipitation of the silver iodide and palladious iodide. For these titrations it is necessary to select a definite and permanent hue of the indicator (reddish brown for dilute solutions) in the unknown, then to compare from above, by reflected light, the unknown with a blank, always attempting to make the blank as nearly equivalent to the unknown as possible. A correction is then applied to the unknown for the amount of thousandth-normal potassium iodide required to produce the definite coloration in the blank. The volume of indicator to be used may be from 0.25 to 0.5 cc. while 1 cc. of a 5% gum arabic solution is sufficient.

II. For *tenth-normal* solutions, when 5 cc. of a 5% gum arabic solution are used, no dilution of the liquid is necessary and the end point can easily be obtained with 0.5 to 1 cc. of indicator. However, in those cases where the solutions are colored, the gum arabic may be omitted with good advantage and the end point determined by observing by transmitted light the supernatant liquid for a permanent slight change in the color of the liquid. For these colored solutions a similar check precipitation without any indicator present is helpful but not necessary. When gum arabic is not used, the volume of the indicator should be at least 1 cc. for each 100 cc. of the liquid to be titrated. The correction to be applied for tenth-normal titrations is 0.03 cc. of tenth-normal potassium iodide, the volume required to produce the coloration. It may be noted here that palladious iodide can easily be distinguished in almost any colored solution because of its dark color—dark brown (almost black) in concentrated solutions

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and reddish brown in dilute solutions. If all these recommended conditions are observed the personal factor, it is believed, will play a very small part toward obtaining reliable and satisfactory results.

Summary.

1. The application of palladious nitrate as an indicator for silver titrations has been tested and found to be satisfactory.

2. The sensitiveness of the indicator is little affected by dilution.

3. The stability of palladious iodide is greater than that of ferric sulfocyanate.

4. Excellent reproducibility and a satisfactory accuracy can easily be obtained for both tenth- and thousandth-normal concentrations of silver nitrate.

5. The use of gum arabic to avoid occlusion of silver nitrate and potassium iodide has given very good results and is to be recommended.

6. The application of palladious nitrate as an indicator apparently overcomes difficulties which arise with the Volhard method in the presence of mercury, palladium and other interfering metallic salts.

7. The errors of the method have been discussed.

8. Finally, the ease and rapidity with which the indicator and also the silver nitrate and potassium iodide solutions can be prepared are advantages.

ROCHESTER, N. Y.

OBSERVATIONS ON THE RARE EARTHS. V. HOLMIUM AND DYSPROSIUM.[1]

BY H. C. KREMERS AND C. W. BALKE.

Received November 30, 1917.

CONTENTS.—1. Introduction. 2. Frationation of the Bromates for the Concentration of Holmium and Dysprosium. 3. Fractionation of the Bromates for the Concentration of Holmium. 4. A Study of the Separation of Holmium from Yttrium. 5. Summary.

1. Introduction.

This investigation has had in mind a twofold purpose. The preliminary part of the work has had in view the development of better and more rapid methods of separation of the rare earth elements, since this is the most difficult portion of all rare earth work. Many of the rare earths have never been obtained in a pure state and it is, therefore, highly desirable to obtain methods of separation more nearly quantitative in nature. Accordingly, the yttrium group has been studied with attention directed toward a contentration of dysprosium and holmium and the separation of holmium from yttrium.

[1] Part of a thesis submitted by H. C. Kremers to the graduate school of the University of Illinois as partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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The second object in view in this investigation[1] was to obtain dysprosium material of a high state of purity having in mind a further study of its atomic weight. The dysprosium material used together with the material used in the study of the separation of holmium from yttrium was obtained from a previous investigation.[2] All of the material used was originally obtained from xenotime and gadolinite. These minerals were pulverized to pass a 100-mesh screen and decomposed with hydrochloric acid. The resulting rare earth chlorides were precipitated with oxalic acid and washed to remove the iron and beryllium in the case of the gadolinite. Another oxalate precipitation was usually resorted to remove all of the iron, silicia, etc. Since the most efficient preliminary separation of the yttrium group earths was found to be the bromates,[3] the earths were converted to the bromates as follows: The oxalates were moistened with concd. sulfuric acid and ignited to 400° in order to remove the excess of sulfuric acid. The anhydrous sulfates were then converted to the bromates by double decomposition with barium bromate. With the exception of the earths obtained from the gadolinite this preliminary fractionation had already been carried out before the present investigation was undertaken. The gadolinite material contained some 5 to 10% of cerium group earths.

2. Fractionation of the Bromates for the Concentration of Holmium and Dysprosium.

Some 12 kg. of rare earth oxalates obtained from part of 100 pounds of gadolinite were converted to the bromates as already described. These bromates were run through 50 recrystallizations in 3 parallel series. The 3 series showed a concentration of samarium, neodymium and praseodymium toward the insoluble end, dysprosium and holmium in the central portion and yttrium, erbium and thulium toward the soluble end.

At this point the dysprosium-holmium rich material was removed from each of the 3 parallel series and made into 3 new series which were labeled A, B, and C.

Series A was made up of the more soluble fractions of the material removed from the 3 parallel series, and contained dysprosium, holmium, yttrium and erbium. The concentration of erbium and yttrium was sought in this series.

Series B contained the fractions richest in dysprosium and holmium with small amounts of the less soluble neodymium and praseodymium bromates and the more soluble erbium and yttrium bromates. Dysprosium and holmium were concentrated in this series.

Series C was composed mainly of the less soluble bromates and contained, besides the bromates of dysprosium and holmium, terbium, neodymium

[1] "Observations on the Rare Earths, VI," to be published later.

[2] Engle and Balke, THIS JOURNAL, 39, 53 (1917).

[3] James, *Ibid.*, 30, 979 (1908).

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and praseodymium with traces of erbium and yttrium. Praseodymium and neodymium were concentrated in this series.

The 3 series were then fractionated in parallel. The concentration of the earths in the different series was observed and controlled mainly by the change in color although the solutions were frequently examined with the spectroscope. As the dysprosium and holmium bromates became more concentrated toward the less soluble end of series A, these fractions were removed from time to time and placed in series B, uniting them with the fractions which showed a similar color. From series C the more soluble dysprosium and holmium fractions were removed in the same way and added to the fractions in series B which most nearly matched them in color. In the same manner the yttrium and erbium which collected in the soluble end of series B were removed and placed in series A and the neodymium and praseodymium from the less soluble end of series B were added to series C. The 3 series were thus given some 30 recrystallizations which caused most of the dysprosium and holmium together with small amounts of the other earths present to collect in series B. This series was then recrystallized 60 times, several fractions being removed from both the soluble and insoluble ends. The fractions numbering 24 to 38 inclusive indicated the following colors and absorption lines:

Fraction No.	Color.	Absorption.	Earths present.
24	Pink	Nd, Pr, Dy, Ho	Nd, Pr, Dy, Ho
25–28	Flesh	Nd, Pr, Dy, Ho	Nd, Pr, Tb, Dy, Ho, Y
29–30	Yellowish pink	Nd, Pr, Dy, Ho	Nd, Pr, Tb, Dy, Ho, Y
31–32	Cream	Dy, Ho	Dy, Ho, Y
33	Cream	Dy (faint), Ho Er (faint)	Dy, Ho, Er, Y
34–38	Pale pink	Ho, Er	Ho, Er, Y

The equivalents of Fractions 31 and 33 were determined by the permanganate method of Gibbs[1] and gave the values 120.9 and 105.7, respectively. This indicated that Fraction 33 contained some 85% of yttrium. By a comparison of the absorption lines with a set of standard solutions the amounts of dysprosium and erbium in this fraction were estimated to be not more than 2 or 3%. This method was found to be fairly rapid for the concentration of dysprosium and even more satisfactory for holmium. The amount of dysprosium in this series was relatively small.

The sacrifice of material by this method was no greater or even less than in the other ordinary methods of fractionation. By the use of only one series, dysprosium and holmium would concentrate only very slowly, but by the above method the concentration of holmium and dysprosium was found to be more rapid. Considerable trouble was given by the cerium basis bromate[2] which continually separated out as a brown sludge. This

[1] *Am. Chem. J.*, 15, 546 (1893).

[2] James and Pratt, THIS JOURNAL, 33, 1326 (1911).

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had to be filtered off from time to time and caused considerable delay in the fractionation. This experience shows that it is advisable to separate the cerium group earths completely from the yttrium group by the double sodium sulfate separation[1] before the bromate fractionation is begun.

3. Fractionation of the Bromates for the Concentration of Holmium.

In the previous investigations in this laboratory, some 12 fractions of holmium-rich material had been obtained from a large bromate series. This material was composed mainly of holmium and yttrium with small amounts of neodymium, praseodymium, terbium dysprosium and erbium. This series was recrystallized 65 times. Neodymium and praseodymium were frequently removed from the insoluble end and erbium and yttrium were removed at intervals from the more soluble end. Fractions 32 to 53 inclusive indicated the following colors and absorption lines:

Fraction No.	Color.	Absorption.	Earths present.
32–35	Yellow with purple tinge	Nd, Pr, Dy, Ho	Nd, Pr, Dy, Ho
36–38	Creamy yellow	Nd, Pr, Dy, Ho	Nd, Pr, Dy, Ho
39–49	Greenish yellow	Dy, Ho, Er	Dy, Ho, Er, Y
49–53	Pale pink	Ho, Er	Ho, Er, Y

This series contained holmium material with yttrium and traces of dysprosium and erbium.

4. A Study of the Separation of Holmium from Yttrium.

By fractionation of the bromates it was found that holmium and yttrium could be obtained free from the other earths. The bromate method was not found to be at all efficient for the separation of holmium from yttrium, and since considerable holmium-yttrium material was at hand it was decided to study methods for the separation of these two elements.

Fractional Precipitation with Lactic Acid.[2]—It was found that if the hydroxides of the rare earths were dissolved in lactic acid with a very small amount of nitric acid present and the resulting solution diluted and warmed on a steam bath for some hours, a very voluminous precipitate separated out, the composition of which was not determined. This behavior suggested a means for the possible separation of holmium from yttrium by fractional precipitation. Accordingly, 90 g. of moist hydroxide of the holmium-yttrium material having an equivalent of 97.5, were dissolved as described above and diluted to 3 liters. By warming this solution gently a portion of the rare earths was precipitated and filtered out. By repeating this process several times the material was split into seven fractions. Fractions 1 and 7 were analyzed and gave equivalents of 97.2 and 94, respectively. This method was accordingly abandoned, since no appreciable separation had taken place.

[1] Engle and Balke, This Journal, 39, 53 (1917).

[2] Böhm, "Seltene Erden," p. 116.

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Fractional Precipitation with Ammonium Carbonate.—This method was first tried by Dennis and Dales[1] on the yttrium group earths as originally obtained from the mineral sources. Some rapid separations were found to take place. These authors dissolved the earth hydroxides in a strong solution of ammonium carbonate and then partially neutralized the resulting solution with acetic acid until the point of precipitation was reached. A very dilute solution of acetic acid was then dropped in with constant stirring until part of the earths had precipitated. This fraction was then filtered off and the resulting solution again treated in a similar manner.

In the hope that this method would prove to be effective in the present problem 50 g. of moist hydroxides of yttrium-holmium material with an equivalent of 98.5 were accordingly dissolved in ammonium carbonate and fractionally precipitated by the above method. A spectroscopic examination of the fractions indicated no appreciable separation. Fraction 7 gave an equivalent of 101.5. It was evident that this method could thus not be successfully applied to the separation of holmium and yttrium.

Fusion of the Nitrates.—The separation of the earths by fusion of the nitrates depends upon the difference in their electropositive characters.[2] Twenty-five grams of the oxides of the holmium-yttrium material were dissolved in nitric acid and the solution evaporated to dryness. This was then fused until partial decomposition had taken place resulting in the formation of basic nitrates of the least electropositive portions of the mixture. After cooling, the fused mass was treated with water which dissolved the undecomposed nitrates but left the basic nitrates as an insoluble residue. The clear solution was then filtered off forming Fraction A. The basic salt, Fraction B, was again dissolved in nitric acid, evaporated to dryness and fused. Fraction A also was evaporated to dryness and fused. The insoluble portion of Fraction B formed Fraction C and the soluble portion of Fraction B was combined with the insoluble portion of Fraction A and the operation repeated.

After a series of 12 fusions the solutions of the different fractions indicated no appreciable separation by a spectroscopic examination.

According to the classification of the rare earths by Levy,[3] europium, gadolinium, samarium and terbium fall in between yttrium and holmium. Since very pure samarium[4] was at hand, it seemed possible that if this element were mixed with the holmium-yttrium material and the three earths fractionated by the nitrate fusion, the samarium would fall between the holmium and yttrium. The samarium could later be removed from the

[1] THIS JOURNAL, 24, 425 (1902).
[2] Urbain, *Ann. chim.*, 19, Sec. 7, 184 (1900).
[3] S. I. Levy, "The Rare Earths."
[4] Prepared by Mr. A. W. Owens.

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holmium by means of the double sodium sulfate separation. Accordingly, 50 g. of samarium oxide were mixed with 25 g. of holmium-yttrium oxides and this mixture subjected to a series of 31 fusions. The original holmium-yttrium oxides had an equivalent of 98.6. The fractions gave the following absorptions and equivalents:

Fraction	*d*,	*e*,	*f*,	*g–j*,	*k*,	*l*,	*m*,	*n*,	*o*.
Absorption	Sa	Sa	SaHo	SaHo	SaHo	Ho	Ho	Ho	Ho
Atomic wt	...	...	..	..	..	154.21	...	154.68	155.32

Most of the yttrium had concentrated toward the end showing the samarium lines. A very rapid concentration of holmium had taken place. This method was found to be the most efficient thus far tried. Work upon the separation of holmium from yttrium is being continued in this laboratory.

5. Summary.

1. The bromate method of fractionating the yttrium group earths for a more rapid concentration of dysprosium and holmium has been studied, and this method was found to be efficient for the concentration of holmium.

2. Some methods for the separation of holmium from yttrium were also studied. The fusion of the nitrates of a mixture of yttrium, holmium and samarium was found to give a very rapid concentration of holmium.

URBANA, ILLINOIS.

OBSERVATIONS ON THE RARE EARTHS. VI. THE PURIFICATION AND ATOMIC WEIGHT OF DYSPROSIUM.[1]

BY H. C. KREMERS, B. S. HOPKINS AND E. W. ENGLE.

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1. Introduction.

The object of the work described in this paper was to further purify dysprosium material already in a high state of purity. This purification was preliminary to a later object, namely, a further study of the atomic weight of dysprosium by the the use of the oxide-chloride ratio as used by Engle and Balke[2] and by a comparative study of this ratio with other ratios.

[1] Part of a thesis submitted by H. C. Kremers to the Graduate School of the University of Illinois as partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] THIS JOURNAL, 39, 53 (1917).

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2. History of Dysprosium.

Our knowledge of the chemistry of dysprosium is very limited and but little concerning the element is found in the literature. In 1878 Delafontaine[1] announced a new element, philippia, giving a strong absorption band (=451.5). In 1880 Delafontaine found that this band was the same as that described by Soret and Cleve for holmium. During the same year Soret[2] announced that the philippia of Delafontaine and his holmium were the same and that the substance contained one body. In 1880 Lecoq de Boisbaudran[3] by means of several hundred fractionations with ammonia and potassium sulfate succeeded in separating the supposed holmium of Soret into two elements. The element giving the absorption maxima: =753, 475, 451.5 and 429.5 was called dysprosium.

It was not until 1906 that Urbain[4] obtained some 50 grams of dysprosium oxide by fractionation of the ethyl sulfates and nitrates. An extensive study of the absorption spectra of the element was also made by the same author. The present accepted value of the atomic weight of dysprosium was determined by Urbain and Demenitraux.[5] According to these authors the ratio which gave the most concordant results was the transformation of the octohydrated sulfate $Dy_2(SO_4)_3.8H_2O$, into the oxide Dy_2O_3 by ignition at a white heat. As a mean of 12 determinations the value 162.54 was obtained as the atomic weight. Their greatest variation was between 162.29 and 162.75. Some fifteen compounds of dysprosium have been studied by Bourion,[6] Urbain and Jantsch[7] and Jantsch and Ohl.[8] The atomic number of dysprosium, according to the table arranged by Mosley,[9] is 67, placing it between holmium 66, and erbium 68. Dushman[10] states that the order of the atomic numbers of dysprosium and holmium in Mosley's table is apparently the reverse of that of the atomic weights. Harkins and Hall[11] assign 66 as the atomic number of the element. Durrant[12] also assigns the same number to dysprosium.

3. Fractionation of the Bromates for the Purification of Dysprosium.

In the fractional crystallization of the yttrium group bromates, by Engle and Balke,[13] dysprosium bromate was obtained containing one or two per

[1] *Compt. rend.*, **87**, 559 (1878).
[2] *Ibid.*, **91**, 378 (1880).
[3] *Ibid.*, **102**, 1003 (1886); *Chem. News*, **53**, 265 (1886).
[4] *Ibid.*, **142**, 785 (1906).
[5] *Ibid.*, **143**, 598 (1906).
[6] *Compt. rend.*, **145**, 243 (1907); *Ann. chim. phys.*, [8] **21**, 77 (1910).
[7] *Ibid.*, **146**, 127 (1908).
[8] *Ber.*, **44**, 1274 (1911).
[9] *Phil. Mag.*, **27**, 703 (1914).
[10] *Gen. Elec. Rev.*, **18**, 614 (1915).
[11] THIS JOURNAL, **38**, 2 (1916).
[12] *Ibid.*, **39**, 621 (1917).
[13] *Loc. cit.*

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cent. of holmium, small amounts of neodymium, praseodymium and traces of terbium. This series was further fractionated as the bromates, during which time fractions were removed from the insoluble end as the neodymium and praseodymium collected here. As the holmium concentrated toward the soluble end these fractions were removed from time to time. These bromates were run through 125 series of recrystallizations. A careful spectroscopic examination indicated faint traces of neodymium and praseodymium in the least soluble fractions. The color of this oxide was slightly buff. Holmium was found in all of the fractions being more concentrated toward the soluble end. Since the amount of holmium present was estimated to change the atomic weight of the dysprosium no more than two or three units in the second decimal place it seemed that this material was sufficiently pure for an accurate determination of the atomic weight. Accordingly, Samples 7 and 8 (Table of Results) were selected from this series.

The bromate fractionation was not wholly ideal in the final purification of dysprosium; neodymium and praseodymium concentrated slowly toward the less soluble end; and the last traces of holmium were not removed by this method.

4. Fractionation of the Ethyl Sulfates for the Purification of Dysprosium.

It seemed highly desirable that the two ethyl sulfate series, which had been fractionated by Engle and Balke[1] for the separation of dysprosium, be further fractionated with the hope that the last impurities might be removed. It was found that most of the fractions of the two above mentioned series had hydrolyzed during the warm summer months, and the majority of the fractions had to be recovered. The individual fractions were precipitated with oxalic acid, ignited to the oxide and weighed. The calculated amount of ethyl sulfuric acid was added to each oxide and agitated until complete solution had taken place. Absolute alcohol was used as the solvent in the fractionation of these series and the crystallization was allowed to take place in a refrigerator in which the temperature was 9°. By this method a temperature of 30–40° was sufficient to dissolve the crystals and by keeping the fractions at this low and constant temperature during crystallization very little hydrolysis took place.

The first ethyl sulfate series, as left by Engle and Balke contained a fraction of one per cent. of terbium with slight amounts of neodymium and praseodymium toward the less soluble end. Holmium was found in all the fractions. This series was fractionated 65 times. Very nearly all of the neodymium and praseodymium had been removed during this time. A small amount of terbium was still present. The holmium could not be removed by this method.

[1] *Loc. cit.*

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The second ethyl sulfate series contained besides the dysprosium very small amounts of terbium. This series was fractionated in the same manner as the first ethyl sulfate series with the hope that the last traces of terbium might be removed. After 60 recrystallizations it was found that some terbium still remained although a considerable amount had concentrated toward the insoluble end.

A comparison of the bromate and ethyl sulfate methods of fractional crystallization shows that the ethyl sulfates were more efficient for the removal of terbium, neodymium and praseodymium from dysprosium. Neodymium, praseodymium and terbium were removed only very slowly by the bromate method. By neither of the methods could all of the holmium be removed although the bromates were the best suited for this purpose.

5. Preparation of Reagents Used in the Atomic-Weight Determinations.

Water.—The ordinary distilled water was redistilled, after the addition of alkaline permanganate, from the still used in this laboratory for the preparation of conductivity water. The water thus prepared gave no test for chlorine by the most delicate nephelometric test.

Nitric Acid.—C. P. nitric acid was redistilled from quartz apparatus. The middle third was collected in a quartz flask and reserved for use. The acid thus prepared gave no test for chlorine.

Oxalic Acid.—C. P. oxalic acid was dissolved in hot water, filtered and recrystallized twice from conductivity water, containing 10% redistilled nitric acid and lastly from conductivity water. Each yield was drained in a porcelain bowl centrifuge.

Hydrochloric Acid.—Concentrated C. P. hydrochloric acid was heated in a quartz distilling flask and the vapors passed over conductivity water in a quartz flask.

Hydrogen Chloride.—This was prepared by dropping concentrated C. P. sulfuric acid into a concentrated solution of C. P. hydrochloric acid. The gas was dried by passing through two towers, one meter high and 2.5 cm. in diameter, filled with glass beads which were kept moist with conc. C. P. sulfuric acid. The entire apparatus was of glass and was continuous.

Nitrogen.—Air was saturated with ammonia, by bubbling through a wash bottle containing concentrated ammonium hydroxide solution, and passed through a quartz tube filled with copper gauze, heated to redness by means of an electric furnace. This nitrogen was bubbled through dil. sulfuric acid to remove the excess of ammonia. The gas was purified by passing through a train composed of vertical towers 60 cm. high and 2.5 cm. in diameter. The first tower contained solid glass beads moistened with dil. sulfuric acid. The second tower contained glass beads moistened with 5% silver nitrate solution. The third tower contained glass beads

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moistened with C. P. conc. sulfuric acid. The fourth tower contained solid sticks of potassium hydroxide. The fifth tower again contained glass beads and conc. sulfuric acid; and lastly the gass passed through a tube containing glass wool interspersed with freshly sublimed phosphorus pentoxide.

Air.—Air was purified in the same manner as was the nitrogen.

The purifying trains for hydrogen chloride, nitrogen and air were all mounted in a compact form on a wooden frame. All connections were made of glass or ground-glass joints. This apparatus was also used by Engle and Balke[1] in their investigation on the atomic weight of dysprosium.

Silver.—The silver used in this investigation was prepared in essentially the same manner as that used by Richards and Wells[2] in their investigation on the atomic weights of sodium and chlorine.

Thirteen hundred g. of C. P. silver bromide were reduced by a dry fusion, composed of the following charge: 8 parts sodium carbonate, 8 parts potassium carbonate, 3 parts of silver bromide and 1 part of flour. This mixture was fused in fire clay crucibles in a large gas-fired pot furnace. The melt was poured into conical iron molds, the silver buttons collecting in the bottom. These silver buttons were cleaned, etched with nitric acid, washed and dissolved in nitric acid. The silver nitrate was recrystallized 3 times from redistilled nitric acid and conductivity water. The crystals were drained in each case by means of a high-speed centrifuge. The silver nitrate solution was next reduced with freshly prepared ammonium formate and washed several times by decantation. The silver placed in large porcelain crucibles lined with pure carbon[3] was fused in an electric furnace. The silver buttons were carefully cleaned, etched with nitric acid, washed, dissolved in redistilled nitric acid and again reduced with ammonium formate. The reduced silver was washed by decantation with conductivity water and fused in large porcelain crucibles lined with pure lime[3] in an electric furnace. The silver thus obtained was carefully cleaned with a stiff brush, etched, washed and electrolyzed, using a bar of pure silver[4] as the cathode. The fused silver was used as the anode and silver nitrate, made by dissolving some of the fused silver in nitric acid, formed the electrolyte. By carefully regulating the strength of the current a well crystallized deposit of silver was obtained. This electrolytic silver was well washed with conductivity water, dried and fused in large unglazed porcelain boats lined with pure lime. This final fusion was carried out in a porcelain tube electric furnace in an atmosphere of pure hydrogen, prepared from zinc and hydrochloric acid and purified by passing through wash towers containing alkaline permanganate, silver sulfate, solid potas-

[1] *Loc. cit.*

[2] *Pub. Carnegie Inst.*, 28 (1905).

[3] Richards and Wells, *Ibid.*

[4] Sears and Balke, THIS JOURNAL, 36, 833 (1915).

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sium hydroxide and lastly through a quartz tube containing heated platinized quartz, and a tube of glass wool interspersed with freshly sublimed phosphoric anhydride. Bars of silver weighing some 50 g. each were obtained and were carefully cleaned, etched, washed and dried and preserved in a desiccator over solid potassium hydroxide. Before weighing the samples for analysis, these bars were cut into pieces, etched to the desired weight and washed with conductivity water, absolute alcohol and ether and heated to 120° for some minutes.

All vessels used in the preparation of the reagents, described above and in the work following, were of platinum, quartz, or Jena and Non Sol resistance glass.

6. Preparation of Dysprosium Oxide.

The dysprosium oxide for the analysis was prepared as follows: The alcoholic solution of the ethyl sulfates was diluted with water, a few cc. of dil. sulfuric acid added and heated to boiling. All the barium, from the small amounts of barium ethyl sulfate present in the series, was removed as barium sulfate. The dysprosium was then precipitated with oxalic acid. The fractions from the bromate series were first precipitated with ammonia, washed, dissolved in nitric acid and from this point on the purification was the same as that of the material from the ethyl sulfate series. Several alternate precipitations with ammonia and oxalic acid were given to each sample. The ammonia precipitation was carried out by passing ammonia gas over the nitrate solution diluted to one liter and agitated until precipitation was complete. The hydroxides were washed by decantation. When washing was complete the hydroxides were dissolved in nitric acid diluted to one liter and heated to boiling. A hot solution of dil. oxalic acid was added slowly up to the point when precipitation began. By allowing the solution to cool a crystalline precipitate was obtained which was easily washed. After washing the oxalate was dried in an electric oven and ignited in platinum if another ammonia precipitation was desired. Each sample was precipitated 3 or more times with ammonia and usually the same number of times with oxalic acid, the last precipitation always being as the oxalate. The last precipitation in each case was carried out by the use of redistilled nitric acid and conductivity water. The final oxalate was ignited for several hours in platinum in an electric muffle furnace at a temperature of 800° and lastly for an hour at 900°.

7. The Ratio of Dysprosium Sulfate to Dysprosium Oxide.

The ratio mentioned above was used by Urbain and Demenitraux[1] upon whose work the present accepted value is based. A sample of dysprosium was prepared by Engle and Balke in the same manner as prepared by the authors mentioned above. This in brief was as follows: The

[1] *Compt. rend.*, **142**, 785 (1906).

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concentrated sulfate solution was precipitated with a large excess of alcohol. This sulfate was washed with absolute alcohol, dissolved in water and crystallized on a steam bath. The sulfate was dried over sulfuric acid in a desiccator. Urbain and Demenitraux claimed that the pure octohydrated sulfate $Dy_2(SO_4)_3.8H_2O$ was obtained in this way.

An alundum crucible was ignited to constant weight in a platinum wound muffle furnace at a temperature of 1200°, and 1.33843 g. of the sulfate, which had been dried over sulfuric acid for 12 months, was weighed out. This was ignited to constant weight, giving 0.66955 g. as the weight of the oxide. This indicates an atomic weight of 173.291. From this determination it would seem that a partial dehydration of the sulfate had taken place in the desiccator. Hopkins and Balke[1] in their work on the atomic weight of yttrium found that the hydrated yttrium salts were not stable when kept over sulfuric acid, calcium chloride or partially dehydrated yttrium salts. The investigation of the dysprosium sulfate was not carried further since it did not appear that a hydrated sulfate of constant composition could be obtained under the present conditions.

8. The Ratio of Dysprosium Oxide to Dysprosium Chloride.

The method of procedure used here was essentially the same as that used by Egan and Balke[2] in their study of a similar ratio for yttrium. Practically the same apparatus used in this work was used by Engle and Balke[3] in their investigation on the atomic weight of dysprosium. The oxide while still hot from the ignition was transferred to the 25 cc. quartz reaction flask, the caps quickly adjusted on the inlet and outlet tubes and the flask cooled in a desiccator. The flask was hung in the balance case for 3 hours or more and weighed. Just before weighing one of the caps was loosened for a moment to equalize the pressure. The oxide was dissolved by addition of hydrochloric acid and gentle warming. No effervescence or spattering was noticed. The quartz reaction flask was then attached to the purifying train by 2 ground glass joints, one serving as an inlet and the other as an outlet for the gases. The purifying train was so constructed that air, nitrogen, hydrogen chloride or a mixture of any two or all of the gases could be passed into the flask at will. The procedure from this point on was varied somewhat from that used by Engle and Balke. An especially constructed oven made of asbestos wood 0.25 inch thick, was used to heat the flask. The inside dimensions were 4 × 6 × 7 inches and mica windows were placed in two opposite sides. Coils of nichrome resistance wire served as the heating unit and by means of outside resistance any constant temperature up to 360° could be maintained. This oven could be placed around the flask after it was attached to the train,

[1] This Journal, 38, 2332 (1916).
[2] *Ibid.*, 35, 365 (1913).
[3] *Loc. cit.*

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in such a manner that the entire flask together with the inlet and outlet tubes was inclosed and entirely protected from the laboratory gases. The various stages of the dehydration could be observed through the mica windows without disturbing the flask. Air was first passed through the flask while the temperature was 110–115°. When the salt began to crystallize hydrogen chloride was mixed with the air until the salt had completely crystallized and dehydration had begun to take place. The air was now stopped and only hydrogen chloride passed through. At this point Engle and Balke passed nitrogen through the flask together with the hydrogen chloride. It was found that nitrogen could be omitted without any difficulty. As the dehydration took place the temperature was gradually raised to 125–130° and kept at this point until water ceased to escape. The temperature was raised to 200°, at which the last molecule of water of crystallization began to come off, the dehydration becoming complete at 230°. From this point on the temperature was gradually raised to 350° and the oven then replaced by a small muffle furnace. When the temperature had reached a dull red the current of hydrogen chloride was stopped and the chloride fused with the Bunsen flame. In the last 4 determinations the chloride was fused by means of the electric furnace. After the flask had cooled somewhat the hydrogen chloride was replaced by dry air. With the exception of Samples 1 and 2 the exit air, from the displacement of the hydrogen chloride, was finally bubbled through silver nitrate solution until no further test for hydrogen chloride could be obtained. This insured the absence of all hydrogen chloride in the flask. When the flask had cooled to room temperature the outlet tube was first disconnected from the train and the cap adjusted. While the air was still passing the inlet tube was disconnected from the train and the cap quickly adjusted thus preventing the entrance of any moist air. The flask was hung in the balance case for several hours and weighed.

The dysprosium chloride formed in this manner dissolved completely in cold water to a clear solution. The dysprosium chloride solution from a preliminary run gave the following reactions toward several indicators: The solution was basic toward rosalic acid, basic to methyl orange, slightly acidic to congo red, slightly basic to cochineal, neutral to litmus and slightly acidic toward methyl red. These reactions indicated that the hydrogen-ion concentration of the solution[1] was $10^{-5 \text{ or } 6}$.

Nine consecutive determinations were made. Samples 1 and 2 were taken from the soluble end of the second ethyl sulfate series. The oxides were slightly colored.

Sample 3 was taken from near the center of the second ethyl sulfate series. The oxide gave a slightly deeper color than Samples 1 and 2. This deeper color was due to the presence of more terbium.

[1] Washburn, "Principles of Physical Chemistry," 1915, p. 333.

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Samples 4, 5 and 6 were obtained from the second ethyl sulfate series after 60 recrystallizations by Engle and Balke. Sample 5 was ignited at 900° for 8 hours.

Sample 7 was obtained from the less soluble end of the bromate series. The oxide was slightly colored.

Sample 8 was obtained from the middle of the bromate series. The oxide was nearly white showing very little terbium to be present.

Sample 9 was also obtained from the insoluble end of the second ethyl sulfate series of Engle and Balke. After ignition for 8 hours at 850° a light buff-colored oxide was obtained. When this was ignited in pure hydrogen for 3 hours at a temperature of 250°, the oxide became pure white. This indicated that the buff color was due to the terbium, present as a higher oxide. The ignition in hydrogen reduced this terbium to the trioxide Tb_2O_3. The atomic weight of this fraction was not much different from that of the others. By strong ignition in hydrogen a slate-colored oxide was formed which left a black residue upon solution in acids. When ignited at a lower temperature this slate-colored oxide was not formed. Bettendorf[1] described the same phenomenon as taking place when gadolinium oxide, containing traces of terbium, was ignited in hydrogen.

All weighings were made on a Ruprecht balance, used exclusively for atomic weight work. This balance was kept in a special cork insulated room, the temperature of which remained constant to within 2 degrees. All weighings were made by the method of substitution, the tare flask being of quartz similar in size and shape to the reaction flask and differing from it in weight by only a few milligrams. The weights were carefully standardized to 0.01 mg. and all weights were corrected to vacuum standard. The specific gravity of the weights was taken as 8.4, that of dysprosium chloride as 3.67[2] and that of dysprosium oxide as 7.81[3]. The atomic weight of oxygen was taken as 16 and that of chlorine as 35.46. The following values were obtained by this ratio:

Sample.	Wt. of Dy_2O_3.	Wt. of $DyCl_3$.	Ratio Dy_2O_3 : $DyCl_3$.	Atomic weight.
1	0.72974	1.04979	1:1.43859	163.83
2	1.36017	1.95604	1:1.43808	164.05
3	0.69716	1.00255	1:1.43804	164.06
4	1.02493	1.47475	1:1.43887	163.71
5	0.87688	1.26253	1:1.43979	163.31
6	0.69318	0.99677	1:1.43796	163.10
7	1.55248	2.23374	1:1.43882	163.72
8	0.83958	1.20763	1:1.43837	163.92
9	1.56481	2.25129	1:1.43869	163.78
			Mean,	163.83

[1] *Ann.*, 270, 376 (1892).

[2] Burion, *Compt. rend.*, 145, 243 (1907).

[3] Engle and Balke, *Loc. cit.*

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9. The Ratio of Dysprosium Chloride to Silver.

The first application of this ratio to any of the rare earths was by Baxter and Chapin[1] in their determination of the atomic weight of neodymium. Baxter and Stewart[2] also used this ratio in their work on the atomic weight of praseodymium. Some very concordant results were obtained by this ratio. Since anhydrous dysprosium chloride could very readily be obtained it was decided to apply the above ratio to this element also.

A preliminary determination was carried out with the use of some sodium chloride. Sodium chloride was recrystallized 3 times from conductivity water and freshly prepared hydrochloric acid. Each yield was centrifugally drained. A sample of this was fused and weighed, transferred to a glass-stoppered Jena Erlenmeyer flask of 1.5 liters' capacity and dissolved in conductivity water. Silver was weighed out to within a fraction of a milligram of the calculated amount. This was dissolved in pure nitric acid in a 750 cc. Erlenmeyer flask containing a column of bulbs to retain the spray. The silver nitrate solution was diluted and added to the salt solution and the flask shaken for 2 hours in a dark room. On the following day a portion of the clear liquid was tested in the nephelometer and indicated a slight excess of chlorine. The calculated amount of silver was added from a standard solution and the flask allowed to stand for 24 hours when the nephelometer test indicated exact equivalence. In this experiment 2.96480 g. of sodium chloride required 5.47146 g. of silver for complete precipitation, giving 0.54186 for the ratio NaCl : Ag. Richards and Wells obtained the ratio 0.54185.

The anhydrous dysprosium chloride, from the oxide-chloride ratio, was dissolved in the quartz flask and the solution transferred to the Erlenmeyer precipitation flask. Assuming the atomic weight of dysprosium to be 162.5, samples of silver were weighed out being usually within a milligram of the calculated amount. The weighed silver was dissolved as described above, diluted to 400 cc. and added to the dysprosium chloride of about the same dilution. The flask was then shaken for 2 or 3 hours and allowed to stand for 48 hours. The solution was then cooled to nearly 0° in order to reduce the solubility of the silver chloride, and portions tested in the nephelometer. Portions of standard solutions of silver or sodium chloride were added until the nephelometer test indicated equivalence. After each addition of standard solution the flask was shaken for one hour and allowed to stand for 24 hours. In order to determine whether true equivalence was obtained the following experiments were carried out: After equivalence had been obtained in Sample 1, approximately one milligram excess of silver was added and after standing for 24 hours the exact equivalent of

[1] *Proc. Am. Acad.*, 46, 215 (1911); THIS JOURNAL, 33, 1 (1911); *Z. anorg. Chem.*, 70, 1 (1911)

[2] THIS JOURNAL, 37, 516 (1915).

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sodium chloride was added. The following day exact equivalence was again found in the solution. In Sample 2 after equivalence had been obtained one milligram excess sodium chloride was added. After 24 hours its equivalent of silver was added. Equivalence was again obtained in the solution. From the foregoing tests it was proven that true equivalence was obtained in the solutions. In Sample 3 the silver ratio was not obtained because of loss in the transfer of the solution.

The weighings were carried out in the same manner as described under the oxide-chloride ratio. The specific gravity of silver was taken as 10.53 and its atomic weight as 107.88. The following values were obtained by the chloride-silver ratio:

Sample.	Wt. of $DyCl_3$.	Wt. of silver.	Ratio $DyCl_3 : 3Ag$.	Atomic weight.
1	1.04979	1.26301	1:1.20309	162.62
2	1.95604	2.35380	1:1.20334	162.57
3	1.00255	...	.....	..
4	1.47475	1.77504	1:1.20362	162.51
5	1.26253	1.51991	1:1.20386	162.45
6	0.99677	1.20033	1:1.20421	162.38
7	2.23374	2.68806	1:1.20338	162.56
8	1.20763	1.45325	1:1.20339	162.56
9	2.25129	2.70992	1:1.20371	162.49
			Mean,	162.52

Since the chloride-silver ratio gave values considerably lower than the oxide-chloride ratio, an attempt was made to determine whether a constant error existed in either one or both of the ratios studied. The difference in the results might be caused by one or more of the following possibilities:

1. Absorption of hydrogen chloride by the anhydrous dysprosium chloride, thus giving a lower atomic weight with the chloride-silver ratio and a higher value with the oxide-chloride ratio.

2. Volatilization of the dysprosium chloride, thus giving a higher atomic weight with the oxide-chloride ratio without affecting the result with the chloride-silver ratio.

3. Incomplete decomposition of the oxalate in igniting to the oxide. The presence of a small amount of carbonate in the oxide would give a higher atomic weight with the oxide-chloride ratio. This would not effect the chloride-silver ratio.

To determine whether hydrogen chloride was absorbed, a sample of the anhydrous chloride was prepared in the regular way and after fusion the hydrogen chloride was replaced by pure nitrogen. After all traces of hydrogen chloride had been swept out of the flask the chloride was gradually brought up to the fusion point by means of an electric furnace. A current of nitrogen was continually passed through the flask and from the outlet tube was bubbled through silver nitrate solution. As the salt began to

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fuse a gradual evolution of chloride ion was noticed. This slow evolution of chloride ion was not diminished even though the salt was kept fused for 2 hours. Upon solution of the dysprosium chloride in water a slight amount of basic chloride was formed. Since the evolution of chloride ion was not sudden at the point of fusion but began to be evolved gradually after fusion had taken place and continued to be evolved seemed to indicate that the source of the chloride ion was from the decomposition of the dysprosium chloride only.

No deposit of the chloride was noticed in the cooler outlet tube of the flask. Hopkins and Balke[1] found that their anhydrous yttrium chloride did not occlude any hydrogen chloride.

Another sample of oxide was weighed and the chloride dehydrated in the regular way but not fused. The temperature was then kept at 360° for 144 hours while hydrogen chloride was continually passed through the flask. At the end of this time the determination was completed in the regular way. The ratio 1 : 1.43933 was obtained, giving an atomic weight of 163.509. This indicated that there was no volatilization of the chloride at this temperature. Engle and Balke in their determination kept the temperature at this point for 2 hours. In the determinations as described in this paper the temperature was not held at this point for any length of time.

Engle and Balke obtained as a mean of 5 determinations the value 164.228. This value is considerably higher than that obtained in the present work. Incomplete decomposition of the oxalate in ignition to the oxide might account for this high value. The oxide in determination No. 5 of the present work was ignited considerably higher than the other samples and was found to give a much lower atomic weight by the oxide-chloride ratio. Since the values obtained by the chloride-silver ratio were lower than those obtained by the oxide-chloride ratio of both the present and the former investigations, it seemed possible that in neither case had a pure oxide been obtained.

Dr. E. Wichers working in this laboratory on the oxide-chloride ratio for erbium discovered that his erbium oxide contained some carbonate. The dysprosium oxide in the present investigation was tested in a manner similar to that followed by Dr. Wichers. A sample of the oxide was ignited in the regular way for 7 hours at 800° and one hour at 900 degrees. The oxide weighed 0.9299 gram. The oxide was introduced into the flask in the regular way and the flask connected to the train. Previous to this the dil. sulfuric acid in the first tower of the train had been replaced with 10% sodium hydroxide solution and air passed through the train until no test for carbon dioxide could be obtained by passing the exit gases through Geissler bulbs containing lime water. The exit tube from the flask was

[1] THIS JOURNAL, 38, 2333 (1916).

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connected by means of a two-way stopcock to 2 Geissler bulbs containing freshly prepared lime water. Air was passed through for some time and the exit gases passed through one of the Geissler bulbs. No visible precipitate was obtained. The exit gas was now directed through the other Geissler bulb by turning the stopcock. While the air was passing, the inlet tube of the reaction flask was loosened and dil. nitric acid introduced. By allowing the acid to seep through the ground joint a seal was thus made and the slight back pressure in the flask prevented the air from entering. The inlet tube was now replaced and air allowed to pass for one hour. Meanwhile the flask was warmed to 60° and the oxide dissolved. Quite an appreciable precipitate could be noticed in the lime water at the end of this time. From the result of this test it was proven quite conclusively that the oxide as prepared contained some carbonate. This no doubt accounts for the high result obtained by the oxide-chloride ratio.

Since platinum became too volatile and distilled into the oxide when ignited for any length of time above 900° an attempt was made to ignite at a much lower temperature in high vacuo. Accordingly a platinum boat containing the oxalate was placed in a quartz tube and ignited for 8 hours at 700° by means of an electric tube furnace. During this ignition the quartz tube was kept evacuated to less than 1 mm. pressure. The tube was then allowed to cool and dry carbon-dioxide-free air was allowed to enter until atmospheric pressure had been reached. The transfer of the oxide to the reaction flask was made in an air-tight box. This box was made of wood well impregnated with paraffin and contained a sliding plate glass cover. The reaction flask was placed in the box and the end of the quartz combustion tube was fitted into a hole cut in one end of the box. Dry carbon-dioxide-free air was passed into the box for some time and in addition an open dish of solid potassium hydroxide was placed inside to absorb the carbon dioxide. By inserting the hands into rubber gloves fitted into holes cut in the sides of the box the boat could be drawn from the tube and the transfer made with the minimum amount of carbon dioxide present. The value obtained by the oxide-chloride ratio in this case was 167.46 as the atomic weight. Two more determinations were carried out by this modification. In place of the platinum boat an alundum boat of the highest grade alundum was used and a temperature of approximately 950° was maintained in the ignition. The values 164.26 and 167.61 were obtained.

One more modification was tried. Two samples of the oxalate were ignited in an alundum crucible for 10 hours at a temperature of 1000° and the transfer was made in the regular way as described in the former part of this paper. The values obtained were 164.55 and 164.40.

It seems probable that the oxide when allowed to cool absorbs carbon dioxide with extreme rapidity and does not lend itself to the manipulation

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as here used. It also appears that the hot oxide when transferred in the air absorbs enough carbon dioxide to vitiate the results. From the experimental data obtained it seems quite evident that the oxide-chloride ratio cannot be applied to dysprosium by the methods thus far tried. The ratio is accordingly being abandoned in favor of the chloride-silver ratio which has given good results in this laboratory.

10. Summary.

1. Dysprosium material already in a high state of purity was further fractionated as the ethyl sulfates and the bromates. The ethyl sulfates were found to be more efficient for the separation of dysprosium from neodymium, praseodymium and terbium. Neither of the two methods was found efficient for the separation of dysprosium from holmium.

2. The hydrate $Dy_2(SO_4)_3.8H_2O$ was not found to be constant in composition when dried over sulfuric acid.

3. The ratio $Dy_2O_3 : DyCl_3$ was further studied. The value 163.83 as the atomic weight was obtained as the mean of 9 determinations. A study has been made to account for the difference of this value and that of a higher value (164.228) obtained in a previous investigation.

4. In studying the ratio $DyCl_3 : 3\ Ag$ the value 162.52 was obtained as the mean of 8 determinations. A comparative study of the two values has been made to account for the difference in the values obtained by the two methods.

5. The dysprosium oxide as prepared for the oxide-chloride ratio by ignition of the oxalate was found to contain some carbonate. Several different methods for preparing a pure oxide were tried but by no method could concordant results be obtained by the oxide-chloride ratio.

6. The results obtained by the oxide-chloride ratio are accordingly discarded in favor of the results (162.52) obtained by the chloride-silver ratio.

URBANA, ILL.

THE LEAD ELECTRODE.

[SECOND COMMUNICATION.]

BY FREDERICK H. GETMAN.

Received January 28, 1918.

Since the publication of a previous paper[1] on the lead electrode some doubt has arisen as to whether lead really exhibits the phenomenon of allotropy.[2] If the metal does exist in more than one form, each modification should possess its own specific potential, and a careful study of the electromotive behavior of lead electrodes prepared in various different ways should afford valuable evidence as to whether or not allotropes exist.

[1] Getman, THIS JOURNAL, 38, 792 (1916).

[2] Lewis and Brighton, *Ibid.*, 39, 1906 (1917).

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With this end in view and also with a view to determining the normal potential of the lead electrode, the following investigation was undertaken:

Method of Investigation.

In studying the electromotive behavior of lead, the following system was employed:

$$\overset{-}{Pb} \mid 0.1\,M\ KCl\ sat.\ with\ PbCl_2 \overset{\longleftarrow}{\parallel} 0.1\,M\ KCl,\ Hg_2Cl_2 \mid \overset{+}{Hg}$$

The direction of the current outside of the cell is indicated by the arrow. All measurements, except those involved in the determination of the temperature coefficient of the cell, were made at 25°.

Purification of Materials.

Potassium Chloride.—A high grade specimen of potassium chloride which had previously been twice recrystallized from conductance water, was subjected to three successive recrystallizations.

Lead Chloride.—A solution of recrystallized lead nitrate was precipitated with a solution of pure hydrochloric acid with constant stirring. After washing the precipitate nearly free from acid with cold water, it was dissolved in boiling distilled water and allowed to crystallize from solution. The crystals of lead chloride were thoroughly dried and preserved in a desiccator.

Mercury.—Redistilled mercury was washed by repeated spraying through a column of nitric acid (1 : 10) after which it was redistilled by Hulett's method.

Mercurous Chloride.—Pure mercury[1] was dissolved in a deficiency of freshly distilled nitric acid. The solution was poured into a dilute solution of nitric acid and the calomel precipitated by the addition of a solution of pure hydrochloric acid. The calomel was washed repeatedly by decantation with hot water for several hours and then transferred to a filter where the washing was continued until the wash water failed to give an acid reaction. After being dried at 110°, it was preserved in dark bottles.

Lead.—The specimens used were obtained from several different sources and were found to be of a very high degree of purity.

Water.—Ordinary distilled water was used in the early stages of the purification of the materials, while conductance water was employed in all of the final recrystallizations and also in the preparation of all solutions. This latter was prepared by the method of Kendall[2] and in no instance was the conductance found to exceed 3×10^{-6} reciprocal ohms at 25°.

Apparatus.

The measurements of electromotive force were made by means of a Leeds and Northrup potentiometer in conjunction with a sensitive galvanom-

[1] Loomis and Acree, *Am. Chem. J.*, **46**, 596 (1911).

[2] Kendall, THIS JOURNAL, **38**, 2463 (1916).

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eter and a Weston cell recently certified by the Bureau of Standards. All temperatures were measured by means of a thermometer which had previously been carefully compared with a thermometer calibrated by the Physikalische Reichsanstalt.

Preparation of Cells.

Two different types of cell were employed: (*a*) an ordinary H cell, and (*b*) a cell in which diffusion between the calomel and lead electrode compartments could be prevented by means of a stopcock.

The H form of cell was used almost entirely for the study of lead amalgams. Before introducing the solutions, a loose plug of absorbent cotton was placed in the horizontal portion of the cell to minimize diffusion. Into one arm of the cell, mercury, calomel paste and 0.1 *M* potassium chloride saturated with calomel were introduced in the order mentioned, thus forming a 0.1 *M* calomel electrode. Into the other arm of the cell a weighed amount of mercury was introduced and then, after adding sufficient saturated solution of lead chloride in 0.1 *M* potassium chloride to fill the arm up to the horizontal connecting tube, a slow current of pure hydrogen was bubbled through the solution to displace dissolved air. After the gas had been passed through the solution for 10 minutes the requisite weight of pure lead to give an amalgam of the desired concentration was added and the passage of the gas was continued for another interval of 10 minutes. This procedure prevented any oxidation of the amalgam. Connection with the calomel electrode and the amalgam was established by means of platinum wires sealed into glass tubes in the usual manner.

The other type of cell, in addition to the stopcock already mentioned, was furnished with a side tube and stopcocks so that a fresh surface of contact between the solutions could easily be established when desired. The connecting tubes were of sufficiently large bore to eliminate the disturbing capillary effects pointed out by Cumming.[1]

Two calomel electrodes made up from carefully purified materials obtained from different sources, were connected in succession with the half-element containing the Pb electrode.

The saturated solution of lead chloride in 0.1 *M* potassium chloride was obtained by agitating an excess of finely crystallized lead chloride with 0.1 *M* potassium chloride at 25° for 48 hours. Two portions of the solution were then removed and the content of lead chloride determined with the following results: 16.98 and 16.91 millimols per liter. These values are in good agreement with those previously found by Noyes[2] and Von Ende,[3] *viz.*, 16.97 and 16.90 millimols per liter.

[1] Cumming, *Trans. Faraday Soc.*, **8**, 86 (1913).
[2] Noyes, *Z. phys. Chem.*, **9**, 623 (1892).
[3] Von Ende, *Z. anorg. Chem.*, **26**, 151 (1901).

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Experimental Data.

The results obtained with fifteen different lead electrodes are given in the following tables:

TABLE I.

E. M. F. Pb | 0.1 *M* KCl. Sat. PbCl₂. || 0.1 *M* KCl Sat Hg₂Cl₂ | Hg.

No. of electrode.	E. M. F.
	Untreated electrodes.
1	0.5383
2	0.5402
3	0.5383
4	0.5394
5	0.5396
6	0.5395
7	0.5394
8	0.5403
9	0.5388
10	0.5392
11	0.5391
Mean,	0.5393
	Treated electrodes.
12	0.5443
13	0.5472
14	0.5513
15	0.5489
Mean,	0.5479

Electrodes 1, 3, 4 and 5 were cast from the same sample of pure lead, while electrode 2 was cast from an exceptionally pure specimen of lead prepared especially for this investigation. All of the cast electrodes were scraped with a glass plate to remove any film of oxide before placing them in the cells. Electrodes 6, 7 and 8 were prepared by depositing lead electrolytically upon platinum spirals from a solution of recrystallized lead acetate acidified with acetic acid. The weight of the deposits varied from 0.0039 g. to 0.0078 g.

Electrodes 9, 10 and 11 consisted of lead amalgams containing approximately 0.75% of lead. The potentials of these amalgams against a stick of pure lead are given in Table II.

TABLE II.

E. M. F. Pb amalg. | 0.1 *M* KCl. Sat. PbCl₂. | Pb.

No. of electrode.	E. M. F.
	Untreated electrodes.
9	0.0111
10	0.0104
11	0.0132

The values of the e. m. f. given in Table II were added to the corresponding values of the e. m. f. of the amalgam cells to obtain the data recorded

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in Table I for electrodes 9, 10 and 11. Electrodes 12, 13, 14 and 15 were cast from pure lead and were then immersed in Heller's solution for different periods of time. This solution, consisting of 400 g. of lead acetate in 1000 cc. of water to which has been added 100 cc. of nitric acid (sp. gr. 1.16), has been shown by Heller[1] and Cohen[2] to promote the transformation of lead into the modification which is stable at room temperature. The times of immersion of the electrodes were as follows: No. 12, 21 days; No. 13, 14 days; Nos. 14 and 15, 25 days. Before introducing these electrodes into the cell, they were washed in dilute nitric acid, then in conductance water and finally in 0.1 *M* potassium chloride.

The variations of the values of the e. m. f. given in Table I for untreated electrodes are so small that we may conclude that the potential of the electrode is independent of its form, *i. e.*, that whether the metal is cast, deposited electrolytically or dissolved in mercury the value of the e. m. f. will remain the same. On the other hand, the values recorded for treated electrodes not only show a greater variation among themselves, but for each electrode, the corresponding value of the e. m. f. is appreciably higher than any of the values given for untreated electrodes. The mean value of the e. m. f. for cells in which the lead electrode had been treated with Heller's solution was over 8 millivolts higher than the mean e. m. f. of cells in which the lead electrode had not been so treated.

Lewis and Brighton[3] point out that notwithstanding the fact that some of the lead sticks which they used were at least 6 years old they failed to show any difference of potential when measured against a freshly deposited lead tree. This observation is confirmed by the present series of experiments: electrodes 1, 3, 4 and 5 were about 4 years old and yet the value obtained with these are in close agreement with the values obtained with the electrolytically deposited electrodes 6, 7 and 8. As Cohen has frequently pointed out, a metal may remain in a metastable condition for years without undergoing any perceptible transformation, but when placed in a sufficiently concentrated solution of one of its salts the transformation takes place in a relatively short time.

It will be observed that the e. m. f. of cells containing lead electrodes which have been immersed in Heller's solution increases with the time of immersion of the electrode. Not only does the potential of the metal increase with the time of immersion but there is a gradual loss of pliability until at the end of 3 weeks the lead has become decidedly brittle.

Calculation of the Normal Electrode Potential of Lead.

The normal electrode potential of lead may be calculated by the familiar formula

[1] Heller, *Z. phys. Chem.*, **89**, 761 (1915).

[2] Cohen, *Trans. Faraday Soc.*, **10**, 228 (1915).

[3] *Loc. cit.*

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$$E^\circ = (E - 0.0529) + \frac{RT}{nF} \ln c$$

where **E** denotes the observed e. m. f. of the cell, c the concentration of Pb^{++} in the solution of lead chloride and where 0.0529 is the difference of potential between the tenth normal and the normal electrode.[1] The remaining symbols in the equation have their usual significance.

The solubility of lead chloride at 25° is 0.0388,[2] and the corresponding degree of ionization is 0.58.[3]

Hence the solubility product of lead chloride = $0.022504 \times (2 \times 0.022504)^2 = 0.0000456$.

The degree of ionization, α_{25}°, for 0.1 M potassium chloride is 0.78,[2] hence

$$c = \frac{0.0000456}{(2 \times 0.0225 + 0.078)} = 0.003013.$$

Substituting this value of c in the formula for the normal electrode potential, we have

$$E^\circ = (0.5393 - 0.0529) - 0.0295 - \log \frac{1}{0.003013}$$
$$= \mathit{0.4121} \text{ volt.}$$

This result is in close agreement with that of Lewis and Brighton who found the normal electrode potential of lead to be 0.4125 volt. If we take the potential of the normal calomel electrode to be —0.2828 volt against the normal hydrogen electrode as zero,[4] then the normal potential of the lead electrode referred to the hydrogen electrode will be *0.1293* volt.

The normal potential of the lead electrode as recently determined by Henderson and Stegeman[5] is 0.4696 volt against the tenth-normal calomel electrode. Recalculating this result in terms of the normal calomel electrode we obtain 0.4168 volt, a value appreciably higher than that obtained by Lewis or than that obtained in the present investigation.

Temperature Coefficient and Thermal Data.

By determining the temperature coefficient of the cell

$$Pb \mid PbCl_2, 0.1\ M\ KCl \parallel 0.1\ M\ KCl, Hg_2Cl_2 \mid Hg$$

and substituting the value of dE/dT thus found in the Gibbs-Helmholtz equation

$$E = \frac{Q}{nF} + T\frac{dE}{dT}$$

[1] Lewis, Brighton and Sebastian, THIS JOURNAL, 39, 2255 (1917).
[2] Von Ende, *Loc. cit.*
[3] Lewis and Brighton, *Ibid.*
[4] Lewis, Brighton and Sebastian, THIS JOURNAL, 39, 2259 (1917).
[5] Henderson and Stegeman, *Ibid.*, 40, 89 (1918).

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the heat of the reaction $Pb + Hg_2Cl_2 = PbCl_2 + 2Hg$ can be readily calculated.

The mean e. m. f. of the cell at 20° was found to be 0.5382 volt and hence the value of dE/dT is 0.00022. Substituting in the Gibbs-Helmholtz equation and solving for Q, we have

$$Q = 2 \times 96500 \times 0.2389(0.5393 - 298 \times 0.00022)$$
$$= 21840 \text{ cal.}$$

This result is in close agreement with the value recently found by Günther,[1] namely 21800 cal.

The heat of formation of mercurous chloride has been determined calorimetrically by both Nernst[2] and Varet[3] who obtained identical results, namely 62600 cal. By combining the preceding thermochemical data, the heat of formation of lead chloride can be calculated in the following manner:

$$Pb + Hg_2Cl_2 = PbCl_2 + 2Hg + 21840 \text{ cal.}$$
$$2Hg + Cl_2 = Hg_2Cl_2 + 62600 \text{ cal.}$$
$$\overline{Pb + Cl_2 = PbCl_2 + 84440 \text{ cal.}}$$

This result agrees well with the following values obtained by direct calorimetric measurement: 83900 cal. (Berthelot), 82800 cal. (Thomsen), and 85570 cal. (Braune and Koref).[4]

Günther[5] from a study of the cell $Pb \mid PbCl_2$ sat. $\| Hg_2Cl_2 \mid Hg$ obtained 85380 cal. for the heat of formation of $PbCl_2$, while Lewis and Brighton obtained 84000 cal. On the other hand, W. C. Lewis[6] employing Haber's equation[7]

$$Q = Nh\,(\Sigma\nu_{\text{resultants}} - \Sigma\nu_{\text{reactants}}),$$

where N is the number of molecules in 1 gram molecule, h the familiar Planck constant, and ν the critical frequency of any given molecular species entering into the reaction, finds the heat of formation of one-gram molecule of lead chloride to be 77660 cal.

The equation of Nernst and Lindemann[8] may be employed to calculate the heat of reaction, U_0, and from this the maximum work A at any desired temperature may be derived. Thus, on integrating the Nernst-Lindemann equation

$$\Sigma nC_p = \frac{dU}{dT} = {}^3/_2 R\Sigma n \left[\frac{(\beta\nu/T)^2 e^{\beta\nu/T}}{(e^{\beta\nu/T} - 1)^2} + \frac{(\beta\nu/2T)^2 e^{\beta\nu/2T}}{(e^{\beta\nu/2T} - 1)^2}\right] + \Sigma nkT^{3/2}, \quad (1)$$

[1] Günther, *Z. Elektrochem.*, 23, 197 (1917).
[2] Nernst, *Z. phys. Chem.*, 2, 23 (1888).
[3] Varet, *Ann. chim. phys.*, 8, 102 (1896).
[4] Braune and Koref, *Z. Elektrochem.*, 18, 818 (1912).
[5] *Loc. cit.*
[6] W. C. Lewis, *J. Chem. Soc.*, 112, 1086 (1917).
[7] Haber, *Ber. Deutsch. physik. Ges.*, 13, 1117 (1911).
[8] Nernst and Lindemann, *Sitz. Preuss. Akad. Berlin*, 1160 (1912).

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we have

$$U = U_0 + {}^3/_2 R\Sigma n \left[\frac{\beta\nu}{(e^{\beta\nu/T} - 1)} + {}^1/_2 \frac{\beta\nu}{(e^{\beta\nu/2T} - 1)}\right] + {}^2/_5 \Sigma nkT^{5/2}, \quad (2)$$

whence we obtain

$$A = U_0 + {}^3/_2 R\Sigma n \left[ln(e^{\beta\nu/T} - 1) - ln(e^{\beta\nu/2T} - 1)\right] - {}^9/_4 R\Sigma n - {}^4/_{15}\Sigma nkT^{5/2}. \quad (3)$$

At 234° A. mercury solidifies so that not only must its heat of fusion, L, be taken into account in our calculations but also the mean specific heat c of liquid mercury from 298° A. to its freezing point. Introducing these additional terms, Equation 2 becomes

$$U_{298°} = U_0 + {}^3/_2 R\Sigma n \left[\frac{\beta\nu}{(e^{\beta\nu/T} - 1)} + {}^1/_2 \frac{\beta\nu}{(e^{\beta\nu/2T} - 1)}\right] + {}^2/_5 \Sigma nkT^{5/2} - nL - nc\,(298\text{–}234). \quad (4)$$

The necessary data for the application of the Nernst-Lindemann equation to the reaction

$$Pb + Hg_2Cl_2 = PbCl_2 + 2Hg$$

is given by Pollitzer[1] and is here reproduced in Table III.

TABLE III.

Substance.	n_1.	$\beta\nu_1$.	n_2.	$\beta\nu_2$.	$k \times 10^5$.
Pb.....	1	92	..	...	7.8
Hg (solid).....	1	97	..	...	21.0
HgCl.....	1	93	1	324	12.0
$PbCl_2$.....	1	85	2	270	18.0

The values of the heat of fusion and of the specific heat of mercury are taken to be 555 and 6.68, respectively. Substituting the above data in Equation 4 and making use of Pollitzer's tables[2] we find $U_0 = 24035$ cal. Introducing this value of U_0 in Equation 3 together with the appropriate data from Table III we find 24041 cal. on solving the equation for $A_{234°}$. Having computed the maximum work at 234° A., the e. m. f. of the cell involving this reaction may be calculated as follows:

$$\mathbf{E} = \frac{24041}{0.2389 \times 2 \times 96500} = 0.521 \text{ volt.}$$

This result is in close agreement with the value obtained experimentally by Pollitzer, *viz.*, 0.525 volt.

Summary of Results.

(1) The e. m. f. of the cell

$$\overset{-}{Pb} \mid 0.1\,M\ KCl \text{ sat. w. } PbCl_2 \parallel 0.1\,M\ KCl, Hg_2Cl_2 \mid \overset{+}{Hg}$$

has been measured at 25° using different lead electrodes; the values of the

[1] Pollitzer, *Z. Elektrochem.*, 19, 523 (1913).

[2] Pollitzer, *Ahren's Samm ung chemischer Vorträge*, 17, 498 (1912).

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e. m. f. obtained with different specimens of lead cast in sticks, with electrolytically deposited lead and with amalgams, were practically identical.

(2) The normal electrode potential of lead was calculated to be *0.4121* volt referred to the normal calomel electrode and *0.1293* against the normal hydrogen electrode.

(3) The values of the e. m. f. of cells containing electrodes which had been immersed for varying periods of time in Heller's solution were found to be uniformly higher than the values obtained with cells containing electrodes which had not been subjected to this treatment.

(4) The heat of the reaction

$$Pb + Hg_2Cl_2 = PbCl_2 + 2Hg,$$

was calculated and found to be 21840 cal., whence the heat of formation of lead chloride was computed to be 84440 cal.

(5) The heat of reaction U_0, and the maximum work $A_{234°}$ were calculated by means of the Nernst-Lindemann equation and the computed value of the e. m. f. at 234° A. was found to be in close agreement with the observed value.

STAMFORD, CONN.

NOTES.

The Oxidation of Sulfides with Potassium Iodate.—In a previous article[1] it was shown that in the oxidation of sulfides with potassium iodate, the amount of sulfur oxidized to sulfuric acid depended on the concentration of hydrochloric acid, and that with an amount of iodate nearly equivalent to the sulfide, the greatest amount of oxidation obtainable with any strength of acid was represented by the equation

$$3MS + 3KIO_3 + 12HCl \rightleftarrows 3MCl_2 + 2S + 3ICl + 5H_2O.$$

We find that if a *large excess* of iodate be used the sulfur may be completely oxidized, whatever the strength of hydrochloric acid provided it be strong enough to prevent the hydrolysis of ICl. This is evidenced by the following analyses:

Freshly prepared hydrogen sulfide water was measured with a 25 cc. pipet into flasks kept at 0°. Some of the samples were titrated with $N/10$ iodine solution and found to contain 0.00154 g. hydrogen sulfide per cc. 100 cc. of 0.05 molar potassium iodate and the desired amount of hydrochloric acid were added to the other flasks and the excess of iodate was titrated with an equivalent iodide solution. The results were as follows:

Normality hydrochloric acid.....	6.40		4.00		3.00	
Iodate used.....	45.32	45.30	45.31	45.28	45.30	45.32

Theory for complete oxidation according to the equation

$$H_2S + 2KIO_3 + 4HCl \rightleftarrows 2ICl + H_2SO_4 + 2H_2O + 2KCl$$

is 45.30 cc.

[1] THIS JOURNAL, 37, 1134 (1915).

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A similar scheme was tried with lead sulfide precipitated from 25 cc. of 0.05 molar lead sulfate in ammonium acetate. 100 cc. of iodate were used as before and the lead sulfide after filtering on asbestos and washing was introduced into the reaction mixture. Theory for complete oxidation of the sulfur requires 50 cc. iodate.

The results were as follows:

Normality HCl	6.50		3.00	
Iodate used	50.02	50.05	50.03	50.05

My thanks are due to Prof. G. S. Forbes for suggestions during the course of this work.

REGINALD S. DEAN.

CHEMICAL LABORATORY OF
HARVARD COLLEGE,
CAMBRIDGE, MASS.

An Accurate Method for Taking "Aliquots" in Volumetric Analysis.—A method for accurately taking "aliquot" portions of a pure substance for use in the standardization of certain volumetric solutions has been recently proposed by C. F. Miller.[1] About five times as much of the standard substance as is required for each titration is weighed out accurately and dissolved in a volume of water slightly exceeding five times the capacity of the pipet to be used. Five equal portions of the solution are then withdrawn, each portion being delivered from the pipet in exactly the same manner. The remainder of the solution together with the rinsings from the pipet, is evaporated in a tared platinum dish, dried, and weighed. The weight of material used for each titration can then be calculated. The method is applicable only with substances which are soluble and which separate again in weighable form on evaporation of the solution. If proper precautions in regard to drying the residue to constant weight are observed, as many weighings and more time are required than with the usual procedure of weighing out separate samples—with no increase in accuracy.

As a matter of fact, occasions where an advantage is to be gained in the standardization of volumetric solutions by a procedure of dividing the initial samples of the pure substances, are infrequent. There are, however, numerous instances in volumetric procedure in which it is desirable to weigh out more of a sample for analysis than is convenient for a single titration. The usual procedure in such a case is to take aliquot portions of the solution of the sample, or of a filtrate or precipitate obtained therefrom, with the use of graduated flasks and pipets. Even if these have been carefully calibrated, this method is not entirely satisfactory because of temperature fluctuations and unavoidable errors in manipulation.

The present writer proposes a procedure, suggested by the one described above, which, in addition to being simpler, more rapid, and more accurate

[1] THIS JOURNAL, 39, 2388 (1917).

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than Miller's method, can be used in either standardization or analysis, with substances which are soluble in any manner and which do not necessarily separate in weighable form from the solution on evaporation. The sample is weighed out, dissolved in water or suitable reagent, and equal portions of the solution are withdrawn in the manner outlined above; the equal portions and also the remainder, including the rinsings from the pipet, are then titrated. The result may be calculated as follows: If W is the weight of the original sample, n the number of equal portions taken,[1] w the weight of sample in each of these portions, a the average number of cc. required for the titration of each portion, and r the number of cc. required for the remainder, then

$$nw + rw/a = W, \text{ or } w = aW/(an + r).$$

In standardization procedure, letting s represent the weight of the standard substance required for 1 cc. of N solution, we have for the normality factor of the solution

$$N.\,F. = w/sa = W/s(an + r);$$

or in analysis, if x is the weight of the substance X required for 1 cc. of N solution, we should have

$$\%\,X = 100\,(N.\,F.)\,xa/w = 100\,(N.\,F.)\,(an + r)\,x/W.$$

It is evident that the result in either standardization or analysis is the average of the titrations used in computing a, but since it depends entirely on the one initial weight W of substance taken, we have in reality only one carefully obtained value. To insure the discovery of a possible error in weighing or recording of weights, or variation in the sample, a duplicate series of titrations should be made with another weighed portion of the substance.

The use of the procedure described to replace in general the usual standardization or analytical procedure of weighing out separate samples, is by no means desirable. In instances of standardization, however, in which the weight required for a single titration is small and consequently the error in weighing may be relatively large, an increase in accuracy is obtained. In analysis when it is desired to take a larger sample of the material than is required for a single titration, the method makes possible the same or an even greater degree of accuracy without the use of calibrated flasks and pipets than is obtained with the usual procedure when carefully calibrated instruments are employed. Even when these are at hand, the extra titration involved in the procedure described (to determine r) is no more

[1] It is obvious that the weight of material and the volume of the solution can be varied to give any desired number of equal portions; also that the titration of only such a number of these portions need be completed as are required to determine a within the limits of error.

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time-consuming than that of allowing the solution to come to a definite temperature and carefully diluting to an exact volume.

HERBERT E. EASTLACK.

DIVISION OF QUANTITATIVE CHEMISTRY,
UNIVERSITY OF ILLINOIS, URBANA.

Detection of Carbon Dioxide in the Analysis of Carbonates or Oxalates.—In testing for carbon dioxide in the qualitative analysis of carbonates or oxalates a convenient method of making use of the calcium or barium hydroxide reagent is indicated in Fig. 1. The novel feature of the method is the tube with a capillary point for containing the reagent.

This capillary point must be fine enough to permit a small quantity of the reagent to remain in the tube without dripping, but not too fine to prevent the passage of gas bubbles upward through the liquid when gentle suction is applied to the open end of the tube. The introduction of the point of the capillary into any space where carbon dioxide may be and the simultaneous aspiration of a few bubbles of the gas in that space into the reagent in the tube will produce the familiar carbonate precipitate with great certainty and delicacy.

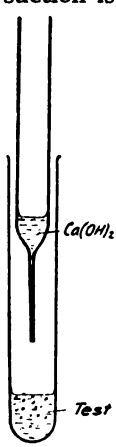

Fig. 1.

The device may be made roughly quantitative for minute quantities of carbonates or oxalates by a slight modification in which the reagent tube containing the lime or baryta water is sealed by means of "de Khotinsky" cement into another similar tube containing the test material as in Fig. 2. By careful aspiration, a drop of 30% sulfuric acid is drawn up into contact with the solid or solution to be tested, after which the aspiration may be continued until the generated carbon dioxide is absorbed by the reagent above. Where oxalates are in question the acid used must carry the necessary amount of permanganate. Parallel tests with similar tubes in which known amounts of a carbonate or oxalate have produced a graduated turbidity standard will, by comparison, give approximately correct quantitative readings with even very minute samples of materials.

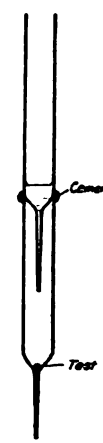

Fig. 2.

O. F. STAFFORD.

CHEMISTRY LABORATORY, UNIVERSITY OF OREGON,
EUGENE, OREGON.

The Extrapolation of Conductivity Data to Zero Concentration.—In a recent issue, Washburn[1] claims to have devised a *new* method for the evaluation of Λ_0, the equivalent conductivity of an electrolyte at zero concentration. Washburn starts with the assumption that "those in-

[1] THIS JOURNAL, 40, 128 (1918).

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fluences which cause a strong electrolyte to deviate from the Mass-Action law at high concentrations *gradually and steadily* become smaller and smaller and finally disappear at infinite dilution." The new method then "consists simply in plotting values of K_E, the Mass-Action expression, against corresponding values of the concentration, employing different assumed values of Λ_0, and rejecting those values which cause the curve in dilute solutions to exhibit radical changes in direction."

Reference to the literature will show that this identical method, founded upon precisely the same assumption, was employed by the present writer six years ago,[1] in the determination of the velocity of the hydrogen ion.

Further and extended comment upon Washburn's articles must be postponed until the writer is free to return to pure scientific work.

JAMES KENDALL.

[CONTRIBUTION FROM THE HAHNEMANN MEDICAL COLLEGE AND HOSPITAL OF CHICAGO.]

ON THE DIGESTIBILITY OF BREAD.

III. ERYTHRODEXTRIN IN STARCH HYDROLYSIS.

BY J. C. BLAKE.

Received December 22, 1917.

It was shown in the second paper of this series[2] that amylolytic activity may be followed quantitatively with great facility by the digestion of erythrodextrin to the achromic point. Efforts made to obtain pure erythrodextrin, partly for the purpose of standardizing amylolytic agents and partly for clinical use in this connection, led to some new discontinuous hydrolyses of starch and to some new methods of estimating the relative concentrations of some of its decomposition products. It is believed that as a consequence of this work pure erythrodextrin will soon be prepared.

New Methods of Analysis.

The relative concentrations of 4 of the decomposition products present in boiled starch partially hydrolyzed with dil. hydrochloric acid were estimated by reading the colorations given with iodine water of different concentrations against Lovibond color glasses by means of a Duboscq colorimeter. The smallest amount of iodine gives a yellow color, thought to be due to protein.[3] Further addition of iodine gives an orange color, then a red or purple, the red color being due to erythramylum.[4] Further

[1] *J. Chem. Soc.*, **101**, 1279 and 1291 (1912).

[2] THIS JOURNAL, **39**, 315 (1917).

[3] Blake, THIS JOURNAL, **38**, 1247 (1916). It is well known that protein gives a yellow color with iodine, especially well seen with the gluten of bread.

[4] This name, given to this substance by Brücke at the time he named the dextrins (*Ber. Wien. Akad.*, **65**, 126 (1872)), from which he clearly distinguished it, has preference over the name rose-amylose proposed by Day ("Digestibility of Starch," etc., University of Chicago Press, 1908, pp. 37, 41). The name cellulose originally given to it by C. Nägeli ("Die Stärkekörner," Zurich, 1858; *Ber. Akad. München*, 1862, p. 281) is, of

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addition of iodine gives purples, violets and blues, the blue being due to amylodextrin (*infra*). A subsequent addition of iodine gives the red color of erythrodextrin, a very large excess of iodine finally giving the yellow (and red) color of the iodine itself. The color of iodine water is 2 red plus 5 yellow of the Lovibond scale; that is, the red equals 40% of the yellow.

The quantitative estimation of the relative concentrations of these substances is based on the fact that increasing amounts of iodine give in each case a sharp maximum of the color due to each of these four substances. This is shown in the following tables, taken at random from several hundred made in this connection. It should be said that under all the conditions used for the readings recorded in this paper the protein and the erythramylum remain associated with the cell walls of the starch granules in such fashion that they do not pass through an ordinary filter paper. All of the work here recorded was done with 4% Oswego Corn Starch, except where otherwise stated.

TABLE I.—MAXIMA DUE TO PROTEIN (YELLOW) AND ERYTHRAMYLUM (RED).
10 cc. of hydrolysis mixture, unfiltered.

Saturated iodine water. Cc.	Lovibond slides.			Total color.		
	Blue.	Red.	Yellow.	Blue.	Red.	Yellow
1/2	0	2.1	2.7	0	2.1	2.7
2	1.1	4.5	2.2	7.0	27.0	13.2
4	2.9	5.0	2.2	29.0	59.0	22.0
6	5.0	8.0	2.2	50.0	80.0	22.0
11	5.0	5.0	Trace	95.0	95.0	Trace
12 1/2	6.8	5.0	Trace	148.0	86.0	Trace

The maxima of 22 yellow and of 95 red are sharply defined. None of this color is due to free iodine.[1] In fact, no free iodine is present, as free iodine is present only after the blue maximum has been passed (not reached in this table) and the maximum due to erythrodextrin has been nearly reached. The yellow color due to the protein is obscured by the large amount of blue color in the last two readings of the table.

course, unsuitable. Nägeli later called this substance starch cellulose (Czapek, "Biochemie der Pflanzen," **1905**, p. 318. Griessmayer (*Ann.*, **160**, 46 (1871)), called it a dextrin whose iodide forms before the blue iodide of starch. It is the "soluble starch" of Musculus and Gruber (*Bull. soc. chim.*, [2] **30**, 67); the "amylodextrin" of W. Nägeli (*Beiträge zur Näheren Kenntnis der Stärkegruppe*, **1872**, ref. Arthur Meyer, "Untersuchungen über die Stärkekörner," **1895**, p. 27; Czapek, *Loc. cit.*, p. 320; Brown and Morris, *J. Chem. Soc.*, **47**, 527 (1885)). The latter authors sharply differentiate between soluble starch and this amylodextrin of W. Nägeli, whereas Musculus and Meyer (*Z. physiol. Chem.*, **4**, 454 (1880)) conclude that erythrodextrin is a mixture of this "soluble starch" and "dextrin" (achroödextrin)—a pronouncement coloring much of the more recent literature (cf. Meyer and Jacobson, "Lehrbuch der Organischen Chemie," **1913**, pp. 1033–4), and doubtless accounting for the fact that Merck's "highest purity dextrin" is almost free from erythrodextrin.

[1] Free iodine, as here understood, gives a red color when added to erythrodextrin in solution.

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TABLE II.—MAXIMA DUE TO AMYLODEXTRIN (BLUE) AND ERYTHRODEXTRIN (RED).
0.200 cc. of hydrolysis filtrate.

Iodine water. Cc.	Total blue.	Total red.
40	59	11
70	60	25
115	30	22
135	25	20

Here the maxima (60 blue and 25 red) are equally sharp, numerous other readings having shown that there are no other maxima between the readings here recorded. The last reading is appended to show that a very large amount of iodine water does not give an increase in the total red color when much blue is present. Under these conditions the maximum red is attained when the yellow tint first reappears in the solution, a reading for the red greater than the true maximum being obtained only when the yellow due to the free iodine is greater than 15% of the total red color.

Typical readings showing this use of the yellow glass are as follows:

TABLE III.—MAXIMA DUE TO AMYLODEXTRIN AND ERYTHRODEXTRIN WITH EXCESS OF IODINE (YELLOW).
0.500 cc. hydrolysis filtrate.

Iodine water. Cc.	Lovibond glasses.			Total color.		
	Blue.	Red.	Yellow.	Blue.	Red.	Yellow.
5	5.0	2.1	0	50	21	0
8	7.0	5.0	0	63	45	0
10	7.0	6.0	0	74	64	0
13	6.0	6.0	0	66	66	0
17	6.0	7.0	0	60	70	0
21	6.0	8.0	0	58	78	0
26	5.0	6.0	0.5	60	72	6.0

The maxima here (74 blue and 78 red) are sufficiently distinct. Since the red of the iodine water (last reading) equals 40% of the yellow (measured on the Lovibond scale), the error in the red due to the iodine would be 2 out of 72 in this experiment, indicating a true reading of 70. This is thought to be within the experimental error, but whether applied or not, gives a reading distinctly less than the previous reading (78).

In case no blue color is present, the maximum red due to the erythrodextrin is not developed until the yellow due to the iodine equals the total red as shown in the following table, again showing that the blue and yellow largely neutralize each other in solutions when both colors are present:

TABLE IV.—MAXIMUM DUE TO ERYTHRODEXTRIN IN THE ABSENCE OF AMYLODEXTRIN.
0.100 cc. hydrolysis filtrate.

Iodine water. Cc.	Lovibond glasses.			Total color.			Total red minus 40% of total yellow.
	Blue.	Red.	Yellow.	Blue.	Red.	Yellow.	
0.51	0	5.0	2.2	0	6.5	2.86	5.5
1.41	0	5.9	5.0	0	9.8	7.5	6.8
2.64	0	5.0	5.0	0	10.0	10.0	6.0
4.47	0	5.0	7.2	0	9.5	14.0	4.0
9.05	0	3.0	5.5	0	13.0	24.0	3.0

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Here the error due to the excess of iodine is material, changing the total red maximum of 10 to 6.8 (last column) as the red due to the erythrodextrin. If still more iodine is added (last reading) the error becomes excessive. No uncertainty for comparative results would be introduced, however, by reading the maximum where the red equals the yellow. No solutions free from amylodextrin are included in the hydrolyses here reported.

A very interesting case is the following, No. 14 of the hydrolysis of boiled starch recorded farther on, in which relatively much erythramylum, little amylodextrin, and much erythrodextrin were present. The readings in this case furnish an excellent test of the method employed, since the red color of the erythramylum tends to merge with the red color subsequently furnished by the erythrodextrin.

TABLE V.—ESTIMATION OF ERYTHRAMYLUM IN THE PRESENCE OF MUCH ERYTHRODEXTRIN.

10 cc. hydrolysis precipitate ("artificial starch") re-suspended in water.

Iodine water. Cc.	Lovibond glasses.			Total color.		
	Blue.	Red.	Yellow.	Blue.	Red.	Yellow.
2.2	0	0.9	0.5	0	9.9	5.5
2.8	0	2.1	0.5	0	25.0	6.0
4.6	0	3.0	0.5	0	31.0	5.0
5.9	1.8	5.0	0.5	26.0	72.0	7.0
7.1	2.9	8.0	0	29.0	80.0	0
11.0	5.0	5.9	0	77.0	91.0	0
15.0	5.0	5.0	0	128.0	128.0	0
19.0	6.1	5.0	0	159.0	131.0	0
22.0	6.8	5.9	0	177.0	153.0	0
26.0	6.8	5.9	0	191.0	165.0	0
30.0	5.0	5.0	0	206.0	206.0	0
35.0	5.0	5.0	0	217.0	217.0	0
42.0	6.1	5.9	0	247.0	239.0	0
49.0	6.8	8.0	0	272.0	320.0	0

Here no maximum in the red appears, and yet 131 was at once taken as representing the erythramylum, because the addition of 4 cc. of iodine water to the solution just previously read gave no material increase in the red coloration (128 to 131), and the subsequent large increase in the red was attributed to erythrodextrin. The value 131 falls on the smooth curve for erythramylum of Fig. 2. Moreover the ratio of iodine water to carbohydrate solution (1.9 : 1) is approximately the same (1.1 : 1) as that used for the maximum color due to erythramylum in Table I, and the difference is primarily due to the larger amount of reducing substances in the solution last reported which act on the iodine. Such a mixture is also obtained by the spontaneous fermentation of cereal starch (but not of potato starch) solutions after about a week, a fact which lead Griessmayer[1]

[1] *Loc. cit.*

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to confound erythramylum with the dextrins. A mixture similar to that recorded in the last table probably lead Musculus and Meyer[1] to the conclusion already expressed, that erythrodextrin is a mixture of "soluble starch" (erythramylum) and achroödextrin.

It should be stated as the most convenient further method of confirmation of these conclusions, both in this case and in all others, that the order of disappearance of these colors when water is added to the mixture is the opposite of that of their appearance, the red color due to erythrodextrin going first, then the blue, then the red of erythramylum, and finally the yellow due to protein. In cases where a large excess of iodine water has been added to a solution containing erythrodextrin and but little amylodextrin, the final color on the addition of water is yellow instead of blue (due to iodine in excess as determined by the odor, the color and the test for free iodine already given).

Temperature of Crystallization of "Artificial Starch."

It is well known that partially hydrolyzed starch partially crystallizes on cooling,[2] the precipitate thus formed being known variously as "artificial starch," "soluble starch" (wholly different from Lintner's "soluble starch," however), and amylodextrin. The temperature at which this crystallization takes place was determined by immersing a thermometer in the solution held in a large test tube to the point at which the crystals were forming. This formation starts at the bottom owing to the fact that the cold liquid accumulates there.

Temperature of Transformation of the Iodides of Amylodextrin and Erythrodextrin.

This temperature was determined in a manner somewhat similar to that used for the determination of the temperature of crystallization, except that in this case the thermometer was held in the upper third of the hot liquid until the blue due to the iodide of amylodextrin or the red due to that of erythrodextrin entirely obscured the yellow color due to the iodine. The temperature at which the iodide first appears varies somewhat with the concentration of the dextrin and greatly with the concentration of the iodine, as is shown by the following results obtained with the filtrate from No. 1 of the hydrolysis of boiled starch reported farther on. The temperature at which the blue iodide appears increases as the concentration of the iodine increases. Since it is nearly constant above 12 volumes of iodine water, 15 volumes were added in making the determinations recorded farther on. The lower temperature obtained in the last reading (No. 1 Series) is due to the great dilution of the dextrin, as confirmed by separate experiments, thus accounting for the temperature of 50° given

[1] *Loc. cit.*

[2] Musculus, *Ann. chim.*, [3] 2, 392 (1874) and ref. cit. in footnote 3; also Meyer u. Jacobson, *Loc. cit.*, pp. 1024. 1032.

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TABLE VI.—TEMPERATURE OF FORMATION OF IODIDES.

Vol. dextrin sol.	Vol. sat. iodine water.	Temp. of formation.
	Filtrate from No. 1.	
1	6	61.5°
1	12	71.5°
1	18	72.5°
1	24	74.0°
1	48	71.5°
	Filtrate from No. 15.	
1	7	57°
1	15	59°
1	30	56°

in Paper I of this series.[1] The results obtained with the filtrate of No. 15, containing erythrodextrin but only a little amylodextrin, the color of the iodides in this case being nearly pure red, show that 15 volumes of iodine water would give practically the maximum temperature at which the iodide forms in all the solutions of the series tested. The decrease in the temperature of formation of this iodide which occurs with dilution of the dextrin (plainly seen in Fig. 2, Nos. 12 to 15) accounts for the temperature of 33° given in the paper last referred to (p. 1251).

"Roasting" Starch Moistened with Dilute Acids.

In approximate agreement with the commercial method of making dextrin, 14.00 g. of Oswego corn starch were moistened with 8.50 cc. of tenth-normal hydrochloric acid and put in an electric oven previously heated and regulated to 85°. The starch was so protected from the source of heat that no considerable differences in temperature could be detected in the region it occupied. The mixture was weighed at the end of 3 and of 4 hours, showing by difference that it had reached constant weight at the end of 3 hours. At intervals of one hour from 3 hours on portions of 1.0000 g. were removed, placed in 12.50 cc. of water and allowed to stand 2 hours, with frequent stirring. The material was then filtered in a Gooch crucible and washed 8 times, with suction to dryness at each washing. Although three washings usually remove all soluble material by this process, yet the eighth wash water still colored blue with iodine, due to the presence of a substance but slightly soluble in water (amylodextrin, pages 631, 635 (3)[2]. The residue was dried at 100° to constant weight. Part of the filtrate (unmixed with wash water) was evaporated to constant weight at 100°, from which the solid contents of the entire filtrate were determined. The filtrate was also polarized on a glucosimeter and its relative content of amylodextrin and erythrodextrin determined by the methods just described, except that Nessler tubes took the place of the colorimeter in this experiment.

[1] The reappearance at 50° of the red color due to erythrodextrin was plainly visible in this solution, due to the great dilution of the blue color by the iodine water.

[2] O'Sullivan, *J. Chem. Soc.*, **35**, 772 (1879).

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TABLE VII.—HYDROLYSIS OF "ROASTED" (85°) ACID-STARCH.

Expt. No.	Time of heating. Hours.	Residue from 1 g. Gram.	Solid contents of filtrate. Gram.	Sum of Cols. 3 and 4.	Polarization on glucosimeter.	Blue for 1 cc. Lovibond scale.	Red for 1 cc. Lovibond scale.
1	3	0.884	0.111	0.995	2.83	17	46
2	4	0.790	0.210	1.000	5.66	17	86
3	5	0.747	0.253[1]	(1.000)	5.76	20	83
4	6	0.651	0.436	1.087	9.60	17	116
5	7	0.591	0.407	0.998	11.48	17	120
6	8	0.712	0.290	1.002	8.40	13	65
7	9	0.663	0.331	0.994	9.92	13	77
8	48	0.514	0.458	0.972	13.40	5	115

These results are plotted in Fig. 1. The fact that the weight of the residue plus the weight of the solid contents of the filtrate equals the weight of the material used for examination (1.000 g.) confirms the weighings and the completeness of the drying, shows that no hydration takes place

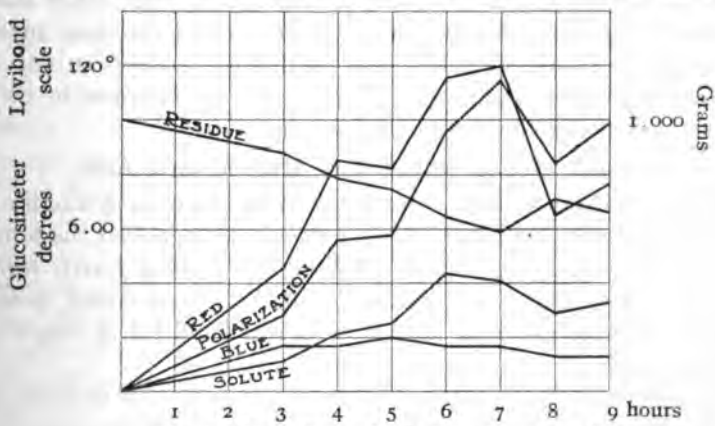

Fig. 1.—Hydrolysis of starch by "Roasting."

during solution of the dextrins (with the possible exception of No. 4) and shows that the extraction was virtually complete (since the wash water was discarded) at the end of 2 hours except for No. 8, in spite of the fact that the wash water still colored blue with iodine.

The general parallelism of the curves for the erythrodextrin (red), for the polarization and for the solid contents of the filtrate offer a confirmation of the general correctness of each of these determinations, especially with regard to their discontinuities. These show clearly the 3 maxima (later shown still more clearly, here shown at the end of 4 hours, 7 hours and 48 hours) due to the decomposition into erythrodextrin of the 3 main polysaccharides of cereal starch (which we have called amylose, amylopectin, and amylocellulose[2]). Further reference to these curves will be

[1] By difference. This material was slightly charred and weighed only 0.202 g.
[2] *Loc. cit.*, Paper I.

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made in the next section. Here we need only point out in addition to what has been said the cause of the maximum shown by the curve for the residue at the end of 8 hours and the corresponding minima shown by all the other curves. This maximum is doubtless due to the fact that the disintegration of the amylocellulose has proceeded far enough to enable it to hold the semi-colloidal dextrins from going into solution to some extent (cf. pages 635–6, conclusions 2 and 8). This explanation accounts for the minima of the other curves, a phenomenon sharply to be distinguished from the final minimum obtained by hydrolysis in solution which is due to the hydrolysis of erythrodextrin into achroödextrin (Fig. 2, erythrodextrin curve after 22 minutes). In other words, if this absorption of erythrodextrin by higher polysaccharides had not taken place, no drop in the curve should have occurred at the end of 7 hours, but nearly a horizontal extension like that at the end of 4 hours, showing but slight destruction of the erythrodextrin. From these considerations we derive the conclusion that erythrodextrin is the final product of the hydrolysis of the three main constituents of cereal starch under these conditions (aside from any sugars which may be formed simultaneously), a conclusion confirmed by the slight amount of achroödextrin[1] in the filtrate.

Starch Boiled with Dilute Hydrochloric Acid.

It was found that the addition of water to the starch-acid mixture of the previous experiment before placing it in the oven increased the formation of erythrodextrin. Hence it was thought that boiling starch with acid sufficiently dilute ought to yield erythrodextrin in maximal quantities. Numerous experiments made with this idea in mind led at length to the following results:

Twenty-eight grams of Oswego corn starch, suspended in 60 cc. of water, were added by means of a rotating funnel with bent stem to 620 cc. of water boiling vigorously and rapidly rotating. Under these conditions all of the starch at once forms a homogenous mixture, which soon boils quietly as a glassy paste. At the end of 5 minutes the cells are entirely normal in appearance, and the liquid outside of the cells gives no color with iodine,[2] as may readily be seen under the microscope when iodine water is added in large excess (the starch-iodide coagulates, leaving clear intercellular spaces). At the end of 5 minutes 20 cc. of 1.13 N hydrochloric acid were added through a vertical condenser originally attached to the flask, the boiling was continued and at stated intervals 44.0 cc. (calculated to the room temperature) were blown out of the flask into a large test tube containing 6.00 cc. of 0.52 N sodium carbonate solution (methyl orange indicator). The hydrolysis mixture was, therefore, approximately 0.032 N hydrochloric acid,

[1] Precipitated by 80 to 90% alcohol from the filtrate of 67% alcohol (Paper I, p. 1249).

[2] Cf. C. Nägeli, "Die Stärkekörner," cit., p. 381.

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although the acidity varies somewhat during the progress of the hydrolysis. The alkali used was approximately twice that required to neutralize the hydrochloric acid added, and was sufficient to leave all the final mixtures decidedly alkaline to phenolphthalein. This strength of alkali was used after extended experiments had shown that it gave the best precipitation of "artificial starch" in the early stages of the hydrolysis. The alkali stops the hydrolysis, but a preservative must be added to prevent fermentation (1 cc. of 1% arsenic acid[1] was added to each tube after the first precipitation).

The hydrolysis mixture was blown into the alkali in such fashion as to mix the two liquids as much as possible, and the mixture was then thoroughly stirred with a thermometer until the opalescence disappeared from the upper part of the liquid. This mixture was then allowed to cool spontaneously, and the temperature of crystallization noted, as already pointed out.

The precipitate thus formed, together with cell fragments, more or less swollen at different stages, was allowed to settle for 48 hours, when its volume was determined in terms of the total volume of the mixture (making allowance for the irregularity of the bottom of the test tube).

The supernatant liquid was then closely decanted (by continuous suction) and filtered. In this filtrate the relative concentration of amylodextrin and erythrodextrin were determined as already pointed out and the polarization was observed. In this filtrate, also, the transition temperature of the predominent iodide was determined.

The precipitate was suspended in the original volume of water and again allowed to settle. Since most of the precipitate dissolved under these conditions,[2] the material left (large cell fragments) will be called the residue. The volume of the residue was determined after 48 hours' settling; the supernatant liquid (called the wash water) was filtered off and its relative concentration of amylodextrin and erythrodextrin determined. The wash water, plainly, gives an idea of the composition of the crystalline precipitate, the "artificial starch." The residue, while re-suspended in the wash water before the second filtration, was used to determine the protein and the erythramylum. The results are reported in the following table.

These results are plotted in Fig. 2, with the arbitrary changes in units (volumes) noted there to bring them all on the same scale in the clearest relationship.

We have here a fairly well defined picture of the profound changes taking place in the hydrolysis of starch after the first 4 minutes and up to the time of the formation of achroödextrin as the principal polysaccharide. From

[1] Blake, Paper I, p. 1248.

[2] Cf. O'Sullivan, *J. Chem. Soc.*, 35, 772 (1879).

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TABLE VIII.—HYDROLYSIS OF CORN STARCH AT 100° BY 0.032 *N* HCl.

Expt. No.	Interval. Minutes.	Temperature of crystallization of "artificial starch."	Precipitate after 48 hours. Volume %.	Residue after 48 hours. Volume %.	Filtrate. Polarization, 200 mm. tube.	Filtrate. Blue in 0.500 cc. Lovibond scale.	Filtrate. Trans. temp. of blue iodide.	Filtrate. Red in 0.500 cc. Lovibond scale.	Filtrate. Transition temp. of red iodide.	Wash water. Blue in 1.000 cc. Lovibond scale.	Wash water. Red in 1.000 cc. Lovibond scale.	Residue re-suspended in original volume of water. Erythramylum in 10 cc. Lovibond scale.	Residue re-suspended in original volume of water. Protein in 10 cc. Lovibond scale.
1	4	68.0°	19[1]	4.2[2]	Turbid	95	72.0°	47	50°	30	19	87	6
2	5	68.0	18[1]	5.5	Turbid	88	72.0	49	...	36	17	103	7
3	6	68.0	16[1]	6.6	Turbid	105	71.5	54	...	36	24	132	8
4	7	71.0	18[1]	7.7	Turbid	98	71.2	70	...	39	23	120	7
5	8	72.5	15.0	5.6	Turbid	90	71.0	68	...	30	18	131	7
6	11	71.5	13.2	4.9	Turbid	85	68.5	72	...	27	22	95	22
7	12	71.5	12.8	3.6	10.48	73	69.0	74	...	24	19	87	15
8	13	71.5	13.9	4.0	10.47	75	68.5	75	...	22	22	135	9
9	14	71.0	13.5	4.4	10.42	72	67.0	74	...	14	16	110	7
10	15	71.0	14.2	3.8	10.40	74	68.3	78	...	18	21	115	14
11	20	69.0	..	...	Lost	...	...	...	...	Lost	Lost	...	..
12	22	68.5	13.6	2.6	10.30	38	...	104	63	7	22	136	13
13	23	67.0	13.6	4.2	10.23	20	...	83	62	14	31	135	8
14	24	67.0	13.5	4.2	10.26	16	...	75	61	16	28	131	6
15	30	64.0	12.3	3.5	10.26	8	...	67	59	7	25	82	8

[1] Includes slight amount recovered from filtrate on longer standing.

[2] 10% additional forms on longer standing, making 14%. This additional 10% is plainly part of the precipitate, as distinguished from the residue.

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the similarity of the hydrolysis of boiled and unboiled starch (not detailed here), it seems that no pronounced chemical changes take place during the 5 minutes' boiling with water. One very noteworthy change takes place, however, during the first 4 minutes' boiling with acid of this strength; the viscous substance (amylopectin?) disappears. The loss of viscosity may be more readily followed by the use of acid of much less concentration. Apparently no precipitate will settle out until this viscous substance has been destroyed. It seems that the turbidity destroyed by the alkali in these experiments, mentioned above, is due to the last traces of this sub-

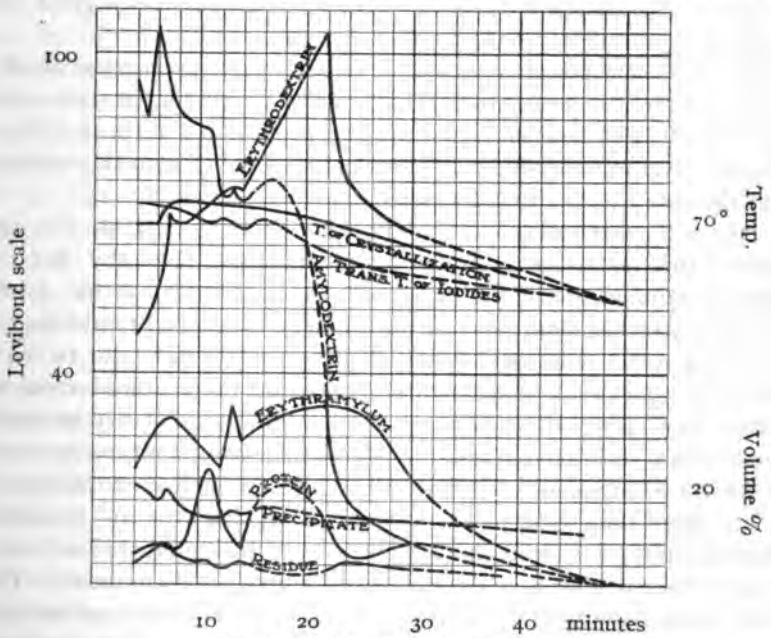

Fig. 2.—Acid hydrolysis of boiling starch.

Erythrodextrin in 0.50 cc. of filtrate.
Amylodextrin in 0.50 cc. of filtrate.
Erythramylum in 2.5 cc. of residue, resuspended in water.
Protein in 10.0 cc. of residue, resuspended in water.

stance. This change is probably concerned with the first maximum and first minimum observed in the blue coloration which iodine produces (amylodextrin curve, 4 and 5 minutes). It should be stated that the extrapolated portions of the curves, represented by dots, are based largely on other concordant experiments and represent the general trend of the curves only. The cell walls are all disrupted in less than one minute after the addition of the acid.

The phenomena really represented in these curves begin with the marked changes which take place between the times 5 minutes and 6 minutes.

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Here the protein reaches its first maximum, the blue reaches its second maximum and the erythramylum has nearly reached its first maximum.

The next minute, 6 to 7, is equally eventful: the erythrodextrin, the erythramylum, the precipitate and the residue reach their first maxima (if we except the initial maximum of the precipitate, which apparently antedates the 4-minute interval at which these curves begin) and the temperature of the crystallization rapidly increases. The sudden and pronounced maximum of the precipitate (at 7 minutes) is plainly due to the almost identical maximum in the residue at the same time, and this is due to some change in the material of the cell walls, as the great development of erythramylum also testifies.

The next few minutes show the rather rapid destruction of all these substances by the further action of the acid. A reading at 9 or 10 minutes would have been helpful in plotting this portion of the curve. The times actually read were around the 3 maxima predicted from other experiments and the results show that the predictions were verified.

The next phenomenon of importance is the remarkable liberation of protein that occurs between 10 and 11 minutes. Here the blue shows a slight maximum, as in the previous case, and again, within 2 minutes, we have another simultaneous maximum of the erythramylum and the erythrodextrin. The smallness of the latter seems to be due to the sharpness of the former, and seems to indicate that the erythrodextrin is a decomposition product accompanying the formation of erythramylum, a conclusion greatly strengthened by the simultaneous appearance of maxima of these two substances in great splendor at the end of 22 minutes.

The third maximum in the protein, interpolated as at 18 minutes, is, unfortunately, uncertain, both by reason of the intermission from 15 to 20 minutes and the early loss of the test started at 20 minutes. This loss is the more regrettable because the possible simultaneous maximum in the blue, which occurred on the two former occasions, is also in doubt. A slight maximum in the blue here is indicated in the projected curve and is also found in the curves of other experiments.

The remarkable constancy of the polarization should be pointed out, the final drop in the curve coming only after most of the erythrodextrin has been hydrolyzed and the concentration of maltose has greatly increased. This observation tends to confirm the commonly accepted opinion that the specific rotatory power of all the common dextrins is the same.

The only other phenomenon which need be pointed out is the maximum in the residue at 23 minutes which accompanies the maximum of the erythramylum at this point, as on two previous occasions. This leaves the slight maximum in the residue at 14 minutes as the only irregularity apparently unrelated to other phenomena. It is, therefore, probably erroneous.

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Conclusion.

It hence appears that boiled corn starch disintegrates in at least three stages, protein and amylodextrin preceding erythramylum and erythrodextrin in order of formation. These three stages probably correspond with those shown by the "roasting" process, the final practical disappearance of the amylodextrin in both cases occurring at the third and greatest maximum of the erythrodextrin. They also probably correspond with the 3 stages of salivary digestion of starch recorded in the first paper of this series.

Subsidiary Findings.

A number of subsidiary findings deserve notice.

1. "Artificial starch," if crystallized out without previous filtration, is a mixture of amylodextrin, erythrodextrin, erythramylum, protein and cell-fragments.

2. "Artificial starch" is a solid solution of amylodextrin and erythrodextrin in higher polysaccharides. This conclusion follows from the observation that the precipitate dissolved in the wash water (Table VII) has the same composition as the mother liquor from which it was originally crystallized, so far as amylodextrin and erythrodextrin are concerned. The ratio of blue to red in both cases is the same, within the experimental error, except in the last 4 readings, where the blue was so small as to render the relation less reliable. Compare finding No. 8, *infra*.

3. Amylodextrin seems to be a pure crystalline substance, moderately soluble in cold water, coloring blue with iodine, the maximum transition temperature of the iodide being 74°. In a mixture this iodide forms after that of protein, after most of the iodide of erythramylum, and before most of the iodide of erythrodextrin. It is precipitated by alcohol of about 40% by volume.

4. Erythrodextrin seems to be a pure substance, tending to intercrystallize with amylodextrin, and hydrolyzing into achroödextrin. It is precipitated by alcohol of 49 to 67% by volume. The maximum transition temperature of its iodide is 64°. It seems to be the final polysaccharide formed in the "roasting" process of manufacturing dextrin when the acid is sufficiently dilute; that is, it is heat stable.

5. Amylodextrin probably hydrolyzes into erythrodextrin, a decrease in this curve corresponding in all cases to an increase in the erythrodextrin curve (Fig. 2).

6. Erythramylum seems to be a pure substance, formed simultaneously with erythrodextrin. Otherwise its relationships to the dextrins are almost wholly unknown, although it probably hydrolyzes slowly into amylodextrin. It may be separated from amylodextrin in solution by precipitation with alcohol of about 35% and it tends to precipitate out of aqueous solution spontaneously on standing. It is obtained in solution only by the almost

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complete disintegration of the walls of the starch granules, as by excessive heat in the roasting process of dextrin manufacture. Its iodide in such a solution is not decolorized by toluene, whereas that of erythrodextrin is readily decolorized by that solvent.

7. In a number of cases long, colorless needles were obtained, probably as a decomposition product of the small amount of cellulose the starch contains. The best crystals were obtained as white needles by adding raw corn starch to boiling 0.011 *N* hydrochloric acid and boiling 150 minutes. At the end of this time the hydrolysis was somewhat more advanced than that represented by the final reading in Table VII, the amylodextrin having just entirely disappeared and the temperature of crystallization having fallen to 45°. At this time, however, these white crystals rather suddenly appeared, of less specific gravity than the (sphero-) crystals previously observed and forming at the constant temperature of 75°. This formation increased steadily in the next 1.5 hours, both crops of crystals being obtained.

8. Lintner's "soluble starch" is nearly pure amylodextrin, formed from the amylocellulose of potato starch and still held in the form of the original cells by a thin layer of insoluble material, which disintegrates in water at about 50°. The transition temperature of its iodide in 1% solution is 69.5°. It crystallizes with difficulty and only at low temperatures (below 50°) even from 10% solution, showing the important role of the higher polysaccharides in the ordinary crystallization of "artificial starch" (cf. Table VII).

HAHNEMANN MEDICAL COLLEGE AND HOSPITAL OF CHICAGO,
CHICAGO, ILL.

[CONTRIBUTIONS FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]

RESEARCHES ON THIOCYANATES AND ISOTHIOCYANATES.

XII. THE POLYKETIDE ISOTHIOCYANATE—ETHYL ISOTHIOCYANPROPIONATE.

BY TREAT B. JOHNSON AND ARTHUR A. TICKNOR.

Received January 2, 1918.

The first polyketide isothiocyanate (mustard oil) to be described in the literature, whose constitution has been definitely established, is ethyl isothiocyanacetate (I), which has been synthezised by Johnson and Hemingway.[1] This is obtained in good yield by the action of thiophosgene on ethyl aminoacetate or its hydrochloric acid salt, while its isomer (II) results by interaction of potassium thiocyanate with ethyl chloroacetate in alcohol solution. Both esters boil at practically the same temperature without appreciable decomposition, and it has been our experience that neither isomer exhibits any tendency to undergo molecular rearrangement

[1] THIS JOURNAL, 38, 1550 (1916).

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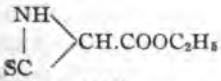
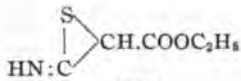
during distillation. Whether the isothiocyanate (II) can be rearranged into the isomeric modification (I) by heating at a higher temperature remains to be established.

$SCN.CH_2COOC_2H_5$ (I). $NCS.CH_2COOC_2H_5$ (II).

In the case of acetic acid only two rhodan derivatives or corresponding esters are to be taken into account, if we exclude from consideration the theoretically possible cyclic combinations represented by Formulas III and IV.

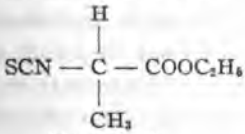


(III).

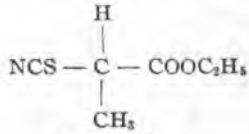


(IV).

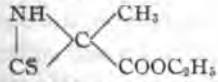
When one considers, on the other hand, the higher homologs of acetic acid a greater number of theoretical possibilities have to be taken into consideration due to the fact that in the α-rhodan derivatives of such acids, we are dealing with combinations containing an asymmetric carbon atom. For example, in the case of ethyl α-rhodanopropionate, we have to deal not only with the two structural thiocyanate isomers represented by Formulas V and VI, but also with the two active modifications of each of these two forms making a total of six isomers conforming to the formula $C_6H_9O_2NS$. Of these six modifications only one has been described in the literature, namely, *dl*-ethyl thiocyanopropionate which was synthesized by Wheeler and Barnes[1] by allowing ethyl α-bromopropionate to interact with potassium thiocyanate. If we take into consideration the theoretically possible cyclic combinations (VII) and VIII), and their respective active modifications then the total number of isomeric ethyl α-rhodonopropionates possible can be increased to twelve. These are represented by the following structural formulas:



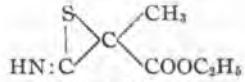
(*d*, *l* and *dl*)
(V).



(*d*, *l* and *dl*)
(VI).



(*d*, *l* and *dl*)
(VII).



(*d*, *l* and *dl*)
(VIII).

It is of interest to note here that both cyclic modifications of ethyl thiocyan- and isothiocyanacetate represented by Formulas III and IV, respectively, contain an asymmetric carbon atom. As far as the writer

[1] *Amer. Chem. J.*, **24**, 76 (1900).

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is aware, there is no series of simple aliphatic compounds containing a single asymmetric carbon atom that presents so many possibilities of structural isomerism as these secondary rhodan combinations.

We have now made a further application of the thiophosgene synthesis of isothiocyanates and found that it is possible to convert the ethylester of alanine smoothly into its corresponding unknown isothiocyanate derivative represented by Formula V. The mustard oil is obtained in good yield by interaction of thiophosgene with the free aminoacid ester as well as with its hydrochloride. Not only have we prepared the racemic modification of this rhodanide, but we have also applied the reaction successfully with the ethyl ester of active alanine and synthesized the *dextro-* modification of the isothiocyanate. The alanine used in this latter work was an active preparation purchased from Kahlbaum and also material which was manufactured for our work by hydrolysis of silk fibroin. Both the *racemic* and *dextro* forms of the isothiocyanates are colorless oils when pure and boil at practically the same temperature, under diminished pressure, as the normal thiocyanate described by Wheeler and Barnes.[1] There is no apparent tendency to undergo rearrangement during distillation in either case.

dl-NCS.CH(CH_3)$COOC_2H_5$.....	Boils at 107–108° at 16 mm.
dl-SCN.CH(CH_3)$COOC_2H_5$.....	Boils at 102–107° at 16–17 mm.
dl-SCN.CH(CH_3)$COOC_2H_5$.....	Boils at 106–108° at 16–17 mm.

As in the case of ethyl isothiocyanacetate the structure of its higher homolog—ethyl isothiocyanopropionate—is established by its behavior towards aniline. We have shown in our previous paper[2] that the isothiocyanacetate and aniline interact with formation of the thiohydantoate $C_{11}H_{11}O_2N_2S$. Fischer[3] applied the reverse reaction by combining phenyl mustard oil with ethyl aminoacetate and obtained the same acyclic derivative. We now find that an entirely different behavior is shown when applying similar reactions with our new isothiocyanate and alanine ester. Aniline and ethyl isothiocyanopropionate combined smoothly as in the case of the acetate combination to form the thiohydantoate represented by Formula IX. When we reversed the procedure and allowed phenyl mustard oil to combine with ethyl α-aminopropionate an entirely different result was obtained, although we apparently worked under practically identical experimental conditions. Here the hydantoate was apparently first formed, but the heat generated by combination was sufficient to cause an inner condensation with production of the cyclic combination 1-phenyl-2-thio-4-methylhydantoin with evolution of alcohol. The changes are represented below:

[1] *Loc. cit.*

[2] Johnson and Hemingway, *Ibid.*

[3] *Ber.*, 34, 440 (1904).

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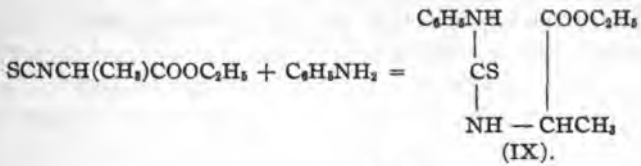
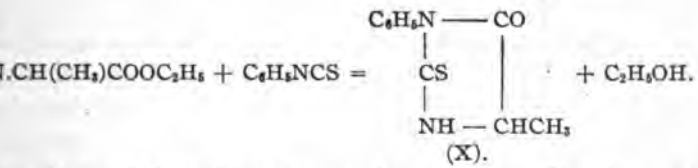


(IX).



(X).

While inactive ethyl isothiocyanopropionate and aniline interacted to give a crystalline thiohydantoate, when the same reaction was applied with the active ester an oil was obtained which showed no tendency to crystallize. In fact a sample of the reaction product was preserved for six months without undergoing any apparent change.

A second reaction which characterized our rhodanide as an isothiocyanate was its behavior towards ethyl alcohol. The two compounds interact smoothly on heating with formation of the thionurethane. This

$$C_2H_5OOC.CH(CH_3).NH.CSOC_2H_5$$

is a representative of a new type of acyclic combinations and is a crystalline combination melting at 55.5–56°.

Our researches on thiocyanates and isothiocyanates will be continued.

Experimental Part.

Preparation of Thiophosgene, $CSCl_2$.—All of this reagent, which we used in this investigation, was prepared by reduction of perchloromethylmercaptan.[1] The chloride was twice distilled and the product used boiled at 72–76°. The yield of thiophosgene was 75% of the theoretical based upon the weight of perchloride taken for reduction.

Preparation of the Ethyl Ester of Alanine and Its Corresponding Hydrochloride.—The most practical method for preparing racemic alanine synthetically in quantity is by application of the synthesis developed by A. Strecker,[2] which is based on the interaction of aldehyde ammonia and hydrocyanic acid in hydrochloric acid solution. Several methods for applying the reaction have been proposed. Heintz,[3] who was the first investigator to use potassium cyanide as a source of the cyanogen in a reaction of this type, showed that the aldehyde ammonia and this salt interact smoothly in an aqueous solution of hydrochloric acid giving good yields of alanine. Ljubavin[4] later modified this procedure by substituting

[1] Johnson and Hemingway, This Journal, **38**, 1550 (1916).

[2] *Ann.*, **75**, 27 (1850).

[3] *Ibid.*, **169**, 120 (1873).

[4] *Zeit. Russ. Chim.*, **12**, 410 (1880); *Zentrbl.*, **1881**, p. 119.

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ammonium cyanide in place of the potassium salt and showed that it interacted smoothly with acetaldehyde in hydrochloric acid solution with formation of the same aminoacid. In other words, the ammonium cyanide played a double role in furnishing both the ammonia and hydrocyanic acid. Later in 1906 Zelinsky and Stadnikoff[1] modified Ljubavin's procedure and showed that the nitrile of alanine results by interaction of potassium cyanide and ammonium chloride with acetaldehyde in aqueous or dilute alcohol solution. This development was continued by Zelinsky, Annenkoff and Kulikoff[2] in 1911. They investigated the reaction of molecular proportions of potassium cyanide and ammonium chloride in aqueous solution with acetaldehyde in ether, and operated as follows:

They added the cyanide solution slowly to a mixture containing the ammonium chloride in water and the aldehyde in ether. After allowing to stand for 40 hours and finally shaking violently for 5 hours they then subjected the aqueous solution to hydrolysis and isolated their alanine in the form of its ethylester. They obtained a yield of 20% of the theoretical. They later found that long standing was unnecessary and showed that by continual shaking and reducing the time of reaction to 15 hours the yield of ester could be raised to 40% of the calculated. The latest paper dealing with this method of synthesis is that contributed by Aschan and Vaskio.[3] They dissolved acetaldehyde in a cold aqueous solution of ammonia, then added slowly potassium cyanide in aqueous solution and finally with cooling a definite amount of conc. hydrochloric acid. After allowing such a mixture to stand for about 12–14 hours it was worked for alanine. The yield obtained is stated to be about 15.8% of the theoretical.

The source of the cyanide radicle in these applications of Strecker's synthesis has been potassium cyanide. Since this is now difficult to obtain it was thought advisable to determine whether the cheaper and readily obtainable commercial sodium cyanide mixture could be employed in its place. A direct comparison in behavior towards acetaldehyde was made experimentally by employing both salts under different but comparable conditions. First, pure aldehyde-ammonia was used; second, pure acetaldehyde was conducted into the cyanide solution to which was added an equivalent amount of ammonia and, third, the entire distillate of crude aldehyde containing alcohol was led directly into the cyanide solution containing ammonia. The acetaldehyde was prepared by oxidizing ethyl alcohol with sodium dichromate and sulfuric acid. In general, 1 kg. of 95% ethyl alcohol with 2 kg. of sodium dichromate, dissolved in 2 kg. of water, reacted with 1.1 kg. of conc. sulfuric acid dissolved in 2 kg. of water to give 305–310 g. of aldehyde-ammonia. The first experiment was con-

[1] *Ber.*, **39**, 1722 (1906).
[2] *Zeit. Physiol. Chem.*, **73**, 459 (1911).
[3] *Ber.*, **48**, 874 (1915).

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ducted with potassium cyanide and was carried out under the following conditions:

Two hundred and fifty g. of acetaldehyde-ammonia was dissolved in a cold solution of 250 grams of ammonium chloride in 850 cc. of water; and then was added slowly, with cooling, a solution of 270 g. of potassium cyanide in 450 cc. of water. The resulting mixture was now allowed to warm to room temperature and finally to stand at ordinary temperature for 24 hours. The solution remained strongly alkaline. It was then acidified strongly with conc. hydrochloric acid, 400–500 cc. of which were required to produce an acid reaction; and the solution finally evaporated to dryness on a steam bath. During the concentration crops of potassium and ammonium chlorides were filtered off by suction and extracted with absolute alcohol to save any alanine hydrochloride present. The final thick, pasty residue of impure alanine hydrochloride was dried as completely as possible and then esterified in the usual way with absolute ethyl alcohol. In order to effect complete esterification the excess of alcohol was removed under diminished pressure and the operation repeated with fresh alcohol. To obtain the free ester of alanine Fischer's method of operating[1] was applied with the modification of salting out the ester with anhydrous sodium carbonate instead of the potassium salt. The method suggested by Zelinsky[2] was not applied. The yield of pure alanine ester obtained was 122 g. boiling at 54° at 17–18 mm. pressure.

In order to determine whether sodium cyanide could be substituted for the potassium salt this experiment was repeated with the following modification in procedure: *i. e.*, 275 g. of the commercial sodium salt, containing cyanide equivalent to that in 98% potassium cyanide, was dissolved in 750 cc. of cold water and substituted for the potassium cyanide. In all other respects, the conditions were the same as in the previous experiment. We obtained 130 g. of the alanine ester boiling at 49–54° at 11–12 mm. pressure. In other words, the yield of alanine was as good as when potassium cyanide was used to furnish the cyanide radicle.

We next conducted experiments to determine whether the amino acid synthesis might be applied successfully without first preparing acetaldehyde ammonia. Pure acetaldehyde gas was passed directly into an aqueous solution of potassium cyanide and ammonium chloride containing an equivalent amount of ammonia. We used 54 g. of potassium cyanide, 50 g. of ammonium chloride, 56 g. of concentrated ammonia solution and 250 cc. of water and an amount of alcohol necessary to produce acetaldehyde equivalent to 50 g. of aldehyde-ammonia. In other respects the operation was the same as before, and we obtained 20 g. of alanine ester boiling at 53–56° at 19–20 mm. and 47–49° at 13 mm. pressure. This experiment

[1] *Ber.*, **34**, 433 (1901).

[2] *Loc. cit.*

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was repeated with substitution of 55.1 g. of commercial sodium cyanide in place of the 54 g. of potassium cyanide. We then obtained 30 g. of the amino acid ester boiling at 47–49° at 10–11 mm. and on redistillation at 48.5–50° at 9 mm. pressure.

Further experiments demonstrated that it was unncessary to purify at all the acetaldehyde for amino acid synthesis. The crude distillate from the oxidation of ethylalcohol was conducted directly into the aqueous solution of sodium cyanide, ammonium chloride and ammonia. Using the same proportions of reacting substances as were employed in the previous experiments and operating under similar conditions we obtained 29.4 g. of alanine ester boiling at 57–61° at 17–18 mm. pressure. In other words, as good a result was obtained as when pure acetaldehyde gas or the aldehyde-ammonia were used. This procedure furnishes a simple and convenient method for preparing alanine ester cheaply from readily obtainable material.

The Hydrochloride of the Ethyl Ester of Alanine.—The hydrochloride of inactive alanine ester was prepared by saturating a dry toluene solution of the amino acid ester with dry hydrogen chloride. It deposited in a crystalline condition and was purified further by crystallization from alcohol. It separated from this solvent as aggregates of hexagonal prisms which melted at 86.5–87° to a clean oil. If this salt is thoroughly dried until free from excess of hydrochloric acid it is not hygroscopic. This salt has previously been prepared by Curtius and Koch[1] from the amino acid by esterification, and after removal of the excess of alcohol to allow the salt to separate. They state that it deposited in the form of clusters of very hygroscopic needles which melted at 64–68°. The results of their analysis indicated that they were dealing with an impure product. They found 24.07% of chlorine, whereas the calculated value is 23.3%. Schmidt and Widman[2] prepared the same salt by passing hydrogen chloride into an ether solution of the ester. They assigned to it a melting point of 69–72°.

Action of Thiophosgene on Inactive Ethyl α-Aminopropionate. Ethyl Isothiocyanopropionate, $SCN.CH(CH_3).COOC_2H_5$.—This new isothiocyanate is formed smoothly by the action of three molecular proportions of the ester of alanine on one mole of thiophosgene, and is obtained as follows:

Seven and one-half g. of thiophosgene is dissolved in 100 cc. of anhydrous ether and 23 g. of the inactive alanine ester added slowly to the cooled solution. The reaction begins immediately and is strongly exothermal. Crystals of the hydrochloride of the aminoester separate almost immediately and the amount formed is practically quantitative, 19.5 g. being attained while theory calls for 19.8 g. This salt melted at 87°. After washing out

[1] *J. prakt. Chem.*, [2] **38**, 472 (1888).

[2] *Ber.*, **42**, 1886 (1909).

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the dissolved hydrochloride of the amino acid ester and finally drying over anhydrous sodium sulfate, the ether is distilled off and the isothiocyanate then purified by distillation under reduced pressure. Eight grams of oil was obtained which boiled at 93.5° to 94.5° at 13 mm. pressure.

The density of the oil was determined by means of a pycnometer and the following values were obtained:

$$D_{40}^{20} = 1.0985 \text{ and } 1.0988$$
$$D_{40}^{20} = 1.1000 \text{ and } 1.1003$$

The index of refraction, which was measured with an Abbé refractometer was found to be as follows: $n_D^{20} = 1.4915$.

Analysis for sulfur (Carius):
0.2057 g. subst. gave 0.2056 g. $BaSO_4$.
Calc. for $C_4H_9O_2NS$: S, 20.15. Found: 20.4.

In one experiment, 4, molecular proportions of the amino acid ester and one equivalent of thiophosgene were taken with the idea of obtaining the corresponding thiourea according to the following equation:

$$CSCl_2 + 2NH_2CH(CH_3)COOC_2H_5 = CS(NHCH(CH_3)COOC_2H_5) + 2HCl.NH_2CH(CH_3)COOC_2H_5$$

Twenty grams of the inactive ester was taken and the operation carried on as in the previous experiment. Thirteen and seven-tenths g. of the hydrochloride of alanine ester separated from the ether while the theoretical yield for one-half conversion to the salt is 13.1 g. The ether solution was washed as usual, dried and the ether finally evaporated, when a dark red oil was obtained which was subjected to distillation in a vacuum. With the oil bath at 160–170° a light yellow oil distilled over at 92.5–93° at 12 mm. and 94–98° at 14 mm. pressure, but during this time there was continuous decomposition and this increased as the temperature was raised. The residue left behind was very dark colored and showed no signs of solidifying. It dissolved in ether at once, but when the ether was allowed to evaporate there was no deposit of crystalline material and only a gummy product was obtained. The oil which distilled over during the decomposition was identified as the mustard oil. The weight was about 2–3 g.

Action of Thiophosgene on the Hydrochloride of Inactive Ethyl α-Aminopropionate.—Twenty-six and three-tenths g. of the hydrochloride was suspended in 100 cc. of dry toluene and 24.6 g. of thiophosgene added during the course of 8 hours. The toluene was heated to 100–110° during this addition of thiophosgene and afterwards for a period of 12 hours. The hydrochloride melted in the toluene and separated as a layer of oil on the bottom of the flask. The mixture was heated until the evolution of hydrochloric acid practically ceased when the toluene layer was removed and the excess of thiophosgene and toluene expelled by distillation. The isothiocyanate was obtained as a dark red oil, which was purified by distillation under diminished pressure. The yield of purified prod-

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uct was 10 g. and it boiled at 120.5–123° at 38–39 mm. pressure. This yield corresponds to only 37% of the theoretical. From the oily residue left in the flask we obtained, after making alkaline and extracting with ether, 5.5 g. of alanine ester boiling at 55–56° at 18 mm. pressure.

The refractive index of the mustard oil was found to be $n_D^{20} = 1.4935$ while the determination of density gave the values $d_4^{20} = 1.1060$ and $d_{20}^{20} = 1.1078$.

A sample, which was redistilled and boiled constant at 106.5° at 16 mm. pressure was analyzed for sulfur according to the method of Carius.

0.1518 g. subst. gave 0.2247 g. $BaSO_4$.
Calc. for $C_6H_9O_2NS$: S, 20.15. Found: 20.33.

In a second experiment 163.9 g. of the hydrochloride of ethyl α-amino propionate was taken for reaction and the operation applied as before. We obtained here only 18 g. of the aliphatic isothiocyanate boiling from 102–107° at 16–17 mm. pressure. The residue of oily hydrochloride was very large in this case and on working for ester we recovered 50 g. boiling at 52–53° at 11–13 mm. pressure. The yield of isothiocyanate based upon the amount of ester lost in reaction was only 18% of theory.

Action of Thiophosgene on the Hydrochloride of *d*-Ethyl α-Aminopropionate. The Formation of Dextro-Ethyl Isothiocyanopropionate, (α) $SCN.CH(CH_3)COOC_2H_5$.—The ester hydrochloride used here was prepared by esterification of *d*-alanine which was imported from Kahlbaum in Germany. Twenty-six and three-tenths g. of the *dextro* salt was subjected to the action of thiophosgene under similar conditions as described in the previous experiments and the resulting isothiocyanate purified by distillation. We obtained 11.5 g. of a light red oil which boiled at 100–101° at 11–12 mm. pressure. This corresponds to a yield of 42% of the theoretical.

In a second experiment we used the hydrochloride prepared from active alanine which was obtained by hydrolysis of silk.[1] From 84 g. of this active salt we obtained 25.5 g. of the mustard oil boiling at 107–109° at 12–14 mm. pressure. This yield was poorer, corresponding to about 29% of the theoretical. In a third experiment we used 66 g. of active hydrochloride and obtained 29 g. of the isothiocyanate boiling at 106–108° at 16–17 mm. pressure. This is a yield of 42% of the theoretical.

A determination of the index of refraction gave the following result:

$$n_D^{20} = 1.4935$$

Specific rotation of the isothiocyanate: A benzene solution containing 2.0663 g. of mustard oil in 100 cc. rotated at 20° in 2- and 4-decimeter tubes 1.23° and 2.46° to the right; hence $\alpha_D^{20} = +29.77$. These readings were made with a Schmidt and Haensch Triple Field Saccharimeter and converted to polariscope degrees by multiplying by the factor 34657. This sample of ester used for these measurements was allowed to stand in a stoppered bottle for six months and then redistilled. It boiled

[1] The silk was supplied by Cheney Brothers, Silk Manufacturers, South Manchester, Conn.

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at practically the same temperature as before indicating no decomposition. A determination of the specific rotation was then made with the following result: 2.3783 g. of the oil in 100 cc. of benzene rotated at 20° in 2- and 4-decimeter tubes 1.525° and 3.084° to the right, hence $\alpha_D^{20} = +31.67$ and $+32.07$ or the average specific rotation of $+32.07$.

The refractive index of this particular sample was $n_D^{20} = 1.4925$.

Another measurement of rotation was made using a different sample when we found the following result:

2.1311 g. in 100 cc. of benzene at 20° gave in 2- and 4-decimeter tubes dextro rotations of 1.178° and 2.357°, respectively. Therefore $\alpha_D^{20} = +27.65$. Refractive index (Abbé) $n_D^{20} = 1.4945$.

Sulfur determination (Carius):
0.1501 g. subst. gave 0.2196 g. $BaSO_4$.
Calc. for $C_6H_9O_2NS$: S, 20.15. Found: 20.09.

Action of Aniline on Inactive Ethyl Isothiocyanopropionate. Formation of Ethyl Phenylmethyl-2-thiohydantoate, $C_6H_5NH.CS.NH.CH(CH_3).COOC_2H_5$.—The isothiocyanate displayed its constitution by its reaction with aniline. Two and nine-tenths g. of aniline in 2 cc. of ether was slowly added to a cold solution of 5 g. of the mustard oil in 50 cc. of ether. The solution assumed a light yellow color and much heat was evolved. After standing for 24 hours the ether was evaporated in a current of air when rosets of colorless crystals deposited. These were recrystallized from alcohol and melted at 83–84° to a clear oil. This ester is very soluble in alcohol, benzene and ether but unsoluble in water. The yield was practically quantitative. Nitrogen determination:

Calc. for $C_{12}H_{16}O_2N_2S$: N, 11.08. Found: 11.01, 10.96.

This experiment was repeated by applying the reaction without a solvent. One and two-tenths g. of aniline was mixed with 2 g. of the isothiocyanate when there was an immediate reaction with formation of a thick oil. This finally solidified and when recrystallized from alcohol melted at 83–84° to a clear oil. This same ester is also formed by allowing phenyl mustard oil to interact with inactive ethyl α-aminopropionate in ether solution. By evaporation of ether it was obtained in a crystalline condition and melted after crystallization from alcohol at 83–84°.

Action of Phenylisothiocyanate on Inactive Ethyl α-Aminopropionate. Formation of 1-Phenyl-4-methyl-2-thiohydantoin, $C_6H_5N.CS.NHCH(CH_3)CO$.—While ethyl isothiocyanopropionate and aniline interact, without use of solvents, to form the hydantoate combination, an entirely different result is obtained if the reaction is reversed and phenylisothiocyanate added directly to the ester of the amino acid. Eleven and five-tenths g. of the mustard oil was added slowly to 10 g. of alanine ester well cooled in ice water. There was an immediate reaction on mixing with evolution of much heat and a thick, yellow oil was obtained. This was allowed to stand

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at room temperature when, after 2 hours, crystals began to deposit and within a few hours the whole mass had completely solidified. The product crystallized from hot alcohol and separated on cooling in the form of aggregates of distorted prisms. The yield was nearly quantitative. The hydantoin melted at 183.5–184.5° to clear oil. This hydantoin has been described by Aschan[1] who assigned to it a melting point of 184°.

Nitrogen determination: Calc. for $C_{10}H_{16}ON_2S$: N, 13.59. Found: 13.50.

Action of Phenylisothiocyanate on Dextro-Ethyl α-Aminopropionate.—Nine and two-tenths g. of phenylisothiocyanate was added to an ether solution containing 8 g. of the above ester. There was an immediate reaction with evolution of heat. This was allowed to stand for several hours and the ether then removed in the usual manner. We obtained a thick, viscous oil which showed no signs of crystallizing. In fact, this product remained as an oil after standing in a desiccator for several weeks. We met with a similar experience when we reversed the reaction and allowed aniline to interact with ethyl isothiocyanopropionate in benzene solution. After heating the benzene solution for 2 hours and then removing the solvent we obtained an oil which showed no signs of solidifying on cooling. It remained in this form for 6 months without showing any signs of depositing crystals.

Formation of Thionurethane, $C_2H_5OOC.CH(CH_3)NH.CSOC_2H_5$ by Interaction of Ethyl Alcohol with Ethyl Isothiocyanopropionate.—Five grams of ethyl isothiocyanopropionate was dissolved in 20 g. of absolute alcohol and the solution then heated on the steam bath for about 3 hours. The alcohol was then removed by distillation when the methane was obtained as a viscous oil. We obtained 5.5 g. of this substance which distilled as a yellow oil boiling at 157–159° at 18–19 mm. pressure. On standing at room temperature this oil finally crystallized and on recrystallization from ether or ligroin separated in the form of slender prisms which melted at 55.5–56°. The yield corresponded to 85% of the theoretical.

Calc. for $C_8H_{16}O_2NH$: N, 6.85. Found: 6.83.

The Action of Thiophosgene on Alanine.—All our attempts to prepare isothiocyanopropionic acid by the action of thiophosgene on the amino acid alanine were unsuccessful. The amino acid and thiophosgene were digested together in dry toluene, and the reaction also applied by heating the acid with thiophosgene without solvents, in sealed tubes at 100°, 130°, 140° and 150°, but in no case did we succeed in obtaining a smooth reaction. Much of the alanine was recovered and amorphous or charred products were formed from which it was impossible to isolate definite compounds.

New Haven, Conn.

[1] *Ber.*, **16**, 1544 (1883).

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[CONTRIBUTION FROM THE CHEMICAL DIVISION OF THE NORTH CAROLINA EXPERIMENT STATION.]

CONTRIBUTION TO THE CHEMISTRY OF GOSSYPOL, THE TOXIC PRINCIPLE OF COTTONSEED.

BY FRANK E. CARRUTH.

Received January 14, 1918.

Gossypol is a peculiar coloring matter present in the cotton plant. Apparently it does not belong to any known class of plant pigments. Its relation to cottonseed poisoning has been shown by Withers and Carruth[1] in separate publications on the subject. At present gossypol is of negative economic value, but it is possible that it may prove useful in the future.

Historical.

The first published work on this substance seems to be by F. Kuhlmann.[2] Kuhlmann was attempting to recover fatty acids from the "degras" or "foots" of cottonseed-oil purification. After distilling off most of the fatty acids by superheated steam, a greenish blue mass was left behind, from which he obtained a substance later called "cottonseed blue" by dissolving out the fatty acids with naphtha, to which he gave the formula $C_{17}H_{24}O_4$. This substance prepared by Kuhlmann differs considerably from pure gossypol in composition and properties and perhaps consisted of a mixture of gossypol with its oxidation products and fatty acids.

A substance known as "gossypin" has been prepared from the foots of cottonseed oil. This substance is described[3] as a light brown pungent powder and evidently consisted of gossypol with certain odorous impurities. Probably this description is based on the work of J. Longmore[4] who, however, does not give his substance any name.

Under the title of "Cottonseed Oil, Its Coloring Matter and Mucilage," J. Longmore describes the preparation of the coloring matter from crude cotton oil:

> "Crude cottonseed oil is of an intense ruby, nearly black color due to its holding in solution a powerful vegetable coloring principle. This latter, according to the results obtained by the author, amounts to 10 to 15 pounds per ton of oil... .
>
> This coloring matter has now been isolated by the author with the result of throwing some light on its nature. In the dry state it is a light powder of pungent odor, of a brown earthy color and possesses powerful dyeing properties. A small proportion of it is soluble in water, but the principle bulk dissolves only in alcohol or alkalies. It is quite insoluble in acids."

Longmore employed strong alkalies to salt out the soap in the foots and to keep the gossypol in solution. He isolated the gossypol by adding acid

[1] *J. Agr. Research*, **5**, 261 (1915); *J. Biol. Chem.*, **32**, 245 (1917); *J. Agr. Research*, **12**, 83 (1918), and a fourth paper to appear soon.

[2] *Compt. rend.*, **53**, 444 (1861).

[3] Cf. Julius Wiesner, "Die Rohstoffe des Pflanzenreiches," 1903, 2nd edition, p. 754.

[4] *J. Soc. Chem. Ind.*, **5**, 200–6 (1886).

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to the alkaline solution. He mentions no further purification and it is evident that his product was very impure.

Finally Marchlewski[1] isolated a crystalline product from the "foots" of cottonseed oil by means of a tedious purification process. He named the crystalline substance gossypol from gossyp (ium-phen)ol. His method of preparation is given in the following translation:

"The crude product which was obtained from an English oil manufacturer had already undergone a purification process consisting of the removal of the greater part of accompanying fatty acids in the form of their calcium salts.

It was extracted with ether which dissolved the gossypol, its oxidation products (which give the solution a dark brown, almost black color) and also considerable amounts of impurities. This solution is concentrated. There remains a viscous mass which is added in portions to boiling acetic acid. When solution takes place it is filtered from a small residue and allowed to cool. After some standing a dark brown amorphous mass separates which is again dissolved in acetic acid. After 4 or 5 repetitions one finally obtains microscopic crystals which are dark brown in color, and which represent the still very impure gossypol.

Further purification is best secured as follows: Dissolve the crystalline mass in boiling alcohol and add to the dark brown solution 50% acetic acid until clouding is noticeable. Then the solution is heated to boiling and filtered. After some standing crystals appear which are considerably lighter than the first product. Repeating this process 5 or 6 times finally yields a beautifully crystallized yellow product. Attempts to obtain the gossypol entirely colorless failed. It seems then that the yellow color is inherent although this is not considered as established."

As will be shown later, Marchlewski's "gossypol" was, no doubt, a substance containing one molecule of acetic acid in loose combination with the phenolic body. This compound with acetic acid will be called for convenience gossypol "acetate," and the phenolic body itself *gossypol*.

In a personal communication to the writer, A. G. Perkin states that he had a very large quantity of it in paste form and that Professors Hummel and Knecht carried on experiments in the hope of converting it into a dye of commercial importance but without success. Perkin intended to work with gossypol but refrained when Marchlewski stated that he wished to reserve the subject.

Occurrence.

Gossypol appears to be a constituent of the cotton plant only. It occurs in peculiar glands called "gland dots," "secretion cavities," or "resin glands" which are present in all parts of the plant except the woody tissue. These are 100 to 400μ in diameter and are readily visible to the eye. They appear to be of lysigenous origin, *i. e.*, formed by disintegration of adjacent cells.[2] The author obtained a crude material from an ether extract of the bark which evidently was chiefly gossypol. It was not obtained crystal-

[1] *J. prakt. Chem.*, **60**, 84–90 (1899).

[2] A photomicroscopic study of the formation of these glands has been made by Dr. A. Viehoever and Mr. E. E. Stanford of the Pharmacognosy Laboratory of the Bureau of Chemistry. It is not yet published.

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line. The glands in the root-bark, leaf, petals and boll as well as those of the seed give with concentrated sulfuric acid a characteristic red color from which fact it is inferred that gossypol exists in all these. An excellent description of the cross section of the seed, showing situation of the glands is given in Winton's "Microscopy of Technical Products," p. 365.

A. G. Perkin[1] states that gossypol "is not identical with and does not appear to be allied with the coloring matter of the (cotton) flowers."

Amount Present in Cottonseed.

Analyses of parts of the plant other than the seed have not been made. By two different methods, the amounts of gossypol present in the undried kernels, nearly free from lint and hulls, has been found to be about 0.6%. The highest yield recorded was 0.63%.

Attempts have not been made to study the actual variation in different varieties of the cotton plant, but since all varieties of seed seem to have approximately the same number of glands, it would appear that the gossypol content does not vary to a greater extent than the oil or protein content. Assuming for convenience that 100 g. of fresh raw kernels contain 0.6% gossypol and 33.3% oil, then the ether extract of this material would contain about three times 0.6 or 1.8% gossypol. Since extraction by petroleum ether does not remove gossypol, the residue after extraction by petroleum ether or gasoline would contain about 0.9% gossypol.

Preparation.

The methods which have been used to isolate gossypol from cottonseed are much simpler than the tedious process by which Marchlewski secured it from the "foots" of cottonseed-oil purification. A crystalline product of high purity is secured directly.

Method 1.—It has been found most convenient to use decorticated cottonseed kernels or "meats" which have been passed through rollers to crush the kernels before they are cooked in the oil mill. The kernels are flattened out and in this condition are easily broken up by sifting into smaller particles. The material is passed through a coarse sieve to remove the greater part of the lint and hulls, and then is extracted with petroleum ether or gasoline. For preparation of considerable amounts of gossypol the kernels may be simply percolated with gasoline to remove the greater part of the oil. The resulting material is dried and extracted with ethyl ether. The extract amounts to 2 to 6% of the weight of material extracted according to the thoroughness of previous extraction. The concentrated extract is of a dark cherry-red color if fresh kernels have been used or almost black if from older seeds. These "gossypol extracts" contain about 17% to 50% gossypol. In one case where very fresh kernels were used a considerable part of the gossypol separated out of the "gossypol extract"

[1] *J. Chem. Soc.*, **75**, 825 (1899).

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on standing as a red crystalline powder. The gossypol may be precipitated in brown amorphous flocks by adding petroleum ether, but better yields, practically quantitative, are secured by treating the gossypol extract with $^1/_2$ to $^1/_3$ its volume of glacial acetic acid. On standing several hours or days, or more quickly by warming in the water bath, most of the gossypol separates as the well crystallized gossypol "acetate" containing 10.1% acetic acid of composition. The crystalline paste is then sucked off and washed with small amounts of glacial acetic acid, and then with petroleum ether. For further purification the gossypol acetate thus secured is dissolved in ether and glacial acetic acid—about 10 parts to 1 part of gossypol—is added. The ether is then in part distilled until the gossypol begins to separate readily. By this method the fatty and colored impurities are retained by the solvent, which is not so much the case when Marchlewski's method using alcohol and aqueous acetic acid is followed. The crystalline product in this case contains uniformly 10.1% acetic acid while by Marchlewski's method it tended to vary from 8.5 to 9.6%.

For the preparation of crystalline gossypol from the "acetate" the latter is dissolved in ether and water is added. The ether is distilled leaving the gossypol as crusts floating on the water which contains all the acetic acid. The free gossypol may then be crystallized from alcohol or other suitable solvent.

Method 1a.—In this method the kernels are not previously extracted with petroleum ether, but with ethyl ether only. The evaporated ether extract is treated with acetic acid and allowed to stand until the gossypol "acetate" separates out. This requires a much longer time than in Method 1. The use of 80% and 90% acetic acid is more advantageous than the use of the glacial acid. It was found that 7 parts of 80% acetic acid per 100 of extract gave larger yields than did 90% or 100% acetic acid. Acid weaker than 80% tends to form a separate layer with the extract. By adding 7 parts per 100, heating to 100° to 115° and then setting aside, the separation of the gossypol "acetate" is hastened. Nevertheless, this is very slowly formed, requiring one to three weeks. The yields are poorer on account of the large mass of oil present but from 50 to 80% of the gossypol may be obtained if sufficient time is given. The following table summarizes some data obtained with different dilutions of acetic acid:

TABLE I.

7 parts of acetic acid per 100 parts by volume of ether extract. Time of standing, about 2 weeks. Weights of extracts, about 91 g.

Strength of acid. Per cent.	G. Gossypol "acetate."		
	Heated to 100° before setting aside.		
99.5	0.0742	Heated to 115°.	0.3040
90	0.6286		0.7170
80	1.1996		0.9310

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Method 2.—The basis of this method is the insolubility in oil of the salts of gossypol. This principle is applied commercially in removing the gossypol and other coloring matters from crude cottonseed oil. The extracts (cf. Method 1) of cottonseed kernels are shaken with a slight excess of strong aqueous caustic soda. The sodium salt of gossypol and sodium salts of the free fatty acids are formed and pass into the aqueous layer, while the clear yellow oil rises to the top. The alkaline liquor is neutralized with acid which causes the fatty acids and gossypol to separate as a pasty mass. This mass may be treated with hot acetic acid to cause separation of the gossypol. This method is not satisfactory and is almost useless where much free fatty acid is present in the oil, when a "break" into oily and aqueous layers is greatly retarded. Gossypol quickly oxidizes in alkaline solutions exposed to air. This oxidation, however, may be retarded by adding sodium hyposulfite ("hydrosulfite") $Na_2S_2O_4$.

If little free fatty acid is present in the gossypol extract, the amount of gossypol present may be approximated by the use of standard dilute alkali. Ether and other fat solvents are added, if necessary, to destroy emulsions. Phenolphthalein is used as indicator. The color change occurs in the aqueous layer after the formation of the disodium salt of gossypol.

Method 3.—This method involves the use of aniline as a precipitating agent for gossypol. A very slightly soluble compound,[1] apparently the dianiline salt of gossypol, is formed, which separates out of an oily extract on standing as an orange-yellow micro-crystalline precipitate. Aniline (about 5% of the weight of the extract) is added to an ether extract of cottonseed. The mixture is warmed on the water bath and set aside to stand a week or more. If given sufficient time the yield is practically quantitative and the method has been used to estimate[2] the amount of gossypol in extracts of cottonseed products.

The aniline-gossypol compound is filtered out and washed free from oil, etc., with ether, or with a small amount of ether followed by larger amounts of petroleum ether. It may be purified by recrystallization from aniline.

To prepare gossypol from the aniline compound it is dissolved in hot alcoholic potash to decompose it and the aniline is steam-distilled out. The resultant aqueous solution of potassium "gossypolate" is treated with a pinch of sodium hyposulfite ($Na_2S_2O_4$) in order to reduce any of the blue oxidation product which may be formed. The gossypol is then precipitated in amorphous flocks by acidifying. It may be filtered out or removed from the solution by shaking with ether in a separatory funnel. It may be purified according to Method 1.

[1] This compound was discovered by Dr. J. T. Dobbins working in this laboratory in attempts to prepare "B" gossypol.

[2] This method therefore may be used to approximate the relative toxicity of extracts. (See *J. Biol. Chem.*, 32, 87 (1917).)

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Marchlewski's "Gossypol"—A Molecular Compound of Gossypol and Acetic Acid.

One would not ordinarily expect a substance to crystallize with acetic acid from a mixture of alcohol and 50% acetic acid in which the acetic acid content varied from 20% to 35%. The crystalline product obtained in this way was usually washed with hot water and dried at 100°. Even on heating to 130° or well above the boiling point of acetic acid there was but very slight loss in weight. Later it was established that this substance, gossypol "acetate," does not lose the acetic acid by boiling in water nor in fact readily below temperatures of 180°, at which point the substance decomposes.

This fact was not recognized at first and was not suspected until a series of molecular-weight determinations by the Beckman method with various solvents gave anomalous results. The presence of acetic acid was established by heating the substance in a tube to its melting point or rather to its decomposition point. A black melt was left behind and a condensate having the characteristic odor of acetic acid collected on the tube. The amount of acetic acid present in these earlier preparations was determined by collecting the vapors driven off at 180–200°, or more easily by the method described under determination of the molecular weight by titration of the acid. For the reason that the amount of acetic acid in preparations obtained from alcohol and 50% acetic acid varied slightly (8.5 to 9.5%) and was less than in preparations crystallized from ether and glacial acetic acid, this latter mixture was used as a solvent, yielding a product freer from foreign coloring matter and with a uniform acid content of 10.1%.

Molecular Weight of Gossypol.

It was first sought to determine the molecular weight of gossypol by physical methods. Preparations of gossypol recrystallized from alcohol with the addition of 50% acetic acid were first used. The results with various solvents were not uniform. Thus, while the boiling-point method with ether and acetone indicated a molecular weight of 300 to 350; with alcohol, benzene and carbon tetrachloride, the elevation of the boiling point was abnormally small indicating a much greater molecular weight. The freezing-point method with benzene was unreliable, owing to the slight solubility of the substance in cold benzene. These results led to suspecting the presence of solvent of crystallization. This was found to be the case as previously described. Further molecular-weight determinations with the McCoy apparatus of the gossypol freed from acetic acid gave the following results:

(1) Ether as solvent. Gossypol 1.002 g. Ether 17.73 g. Elevation 0.20°. Molecular weight found: 595.

(2) Acetone as solvent. Gossypol 1.008 g. Acetone 25.6 g. Elevation 0.121°. Molecular weight found: 553.

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(3) Gossypol "acetate" in ether as solvent. Gossypol "acetate" 0.994 g. Ether 20.0 g. Elevation 0.291. Apparent molecular weight found: 352.

These data indicate that the gossypol "acetate" dissociates in solution into free gossypol and acetic acid causing the previously mentioned anomalous results.

Molecular Weight of Gossypol by Chemical Methods—Titration with Standard Alkali.—After it was found that gossypol "acetate" crystallized from ether-acetic acid contained uniformly about 10.1% acetic acid or somewhat more than that prepared in Marchlewski's way, the latter's method was abandoned. Since the determination of acetic acid is easily and accurately made, the method offers a reliable method for the determination of the molecular weight.

Gossypol "acetate" recrystallized 4 times from ether-glacial acetic acid mixture was dissolved in ether. Warm water was then added and the ether driven off. The water was then separated from the brittle crusts of gossypol which remained, the latter dissolved in ether, and the previous treatment repeated. The water containing the acetic acid was then titrated with alkali using phenoltetrachlorophthalein as indicator.

Subst., (I) 0.5326, (II) 0.5057; cc. 0.1 *N* NaOH, (I) 8.98, (II) 8.57.
Acetic acid found: (I) 10.12, (II) 10.17.
Acetic acid calc. for:
(1) Mol. wt. 592 $C_{30}H_{28}O_9.C_2H_4O_2$ 10.18
(2) Mol. wt. 594 $C_{30}H_{30}O_9.C_2H_4O_2$ 10.10

Hence "free" gossypol has a molecular weight of 530 if $C_{30}H_{28}O_9$, or 532 if $C_{30}H_{30}O_9$.

Molecular-Weight Determination by Direct Titration of "Free" Gossypol.—The above values for the molecular weight of gossypol stand in agreement with the values obtained by direct titration of the residual gossypol after removing the acetic acid of combination. The free gossypol left after removal of the acetic acid in the above determinations was dissolved in alcohol and titrated with alkali using phenoltetrachlorophthalein as indicator. Since the gossypol solution is yellow the end point is more difficult to detect.

The weights of gossypol used here were found by subtracting the 10.12% and 10.17% acetic acid from the weights of the gossypol "acetate" used above.

Subst., (I) 0.4787, (II) 0.4543; cc. 0.1 *N* NaOH, (I) 17.6, (II) 17.0.

Hence assuming gossypol neutralizes two equivalents of NaOH the values for the molecular weight are (I) 544, (II) 532.

Concordant results were also obtained by titrating weighed amounts of pure gossypol and of gossypol "acetate." The "acetate," as is evident, neutralizes three equivalents of alkali. While gossypol thus behaves as a fairly strong acid, it is not thought that it contains carboxyl groups since the benzoyl and acetyl derivatives are not soluble in cold dilute aqueous

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alkali. The fact that the disodium salt of gossypol is neutral to phenolphthalein in aqueous solution gives an indication of its relative strength as an organic acid.

Empirical Formula.

Marchlewski[1] made several analyses of gossypol which had been dried under different conditions. Those which had been heated were much higher in carbon. The three determinations on which, together with the analysis of the lead salt, Marchlewski established his formula $C_{15}H_{14}O_4$ (or $C_{32}H_{34}O_{10}$) are given below.

Composition of Gossypol (Marchlewski).

Preparation ash free and dried *in vacuo* over H_2SO_4.

Found: C, 66.5, 66.3, 66.4; H, 6.0, 6.2, 6.1.

Calc. for $C_{15}H_{14}O_4$: C, 66.7; H, 6.0. Calc. for $C_{32}H_{34}O_{10}$: C, 66.4; H, 5.9.

Composition of the lead salt from an alcoholic solution of gossypol and lead acetate. Calc.: C, 35.5; H, 2.7; PbO, 50.8. Found: C, 36.00; H, 3.01; PbO, 51.1.

"Therefore," Marchlewski says, "gossypol contains two hydroxyl groups. Should I succeed in obtaining greater quantities of gossypol in sufficiently pure condition, I will not fail to give this interesting body a thorough study and communicate the results in this place."

Since the following analytical data differ somewhat from those given by Marchlewski, the question arises, are his analyses correct, or did he have a substance which, by reason of the previous treatment of the seed and oil, had undergone a change in composition. Some slight difference is due to the smaller amount of acetic acid probably present in his preparation.

Although evidence shows that considerable alteration in the toxic properties of gossypol takes place in cooking in the oil mill, the changed gossypol ("D" gossypol, see p. 660) does not pass into the oil to any extent, but remains in the press cake, hence it is apparent that Marchlewski did not have "D" gossypol. On the other hand in cold pressing much *unchanged* gossypol passes into the oil.

The following analytical data give results which agree well with the formulas $C_{30}H_{28}O_9$ or $C_{30}H_{30}O_9$ for gossypol.

Analysis of gossypol "acetate" four times recrystallized from ether and glacial acetic acid.

	Subst.	CO_2.	H_2O.	% C.	% H.
	1st crop of crystals.				
1	0.2321	0.5547	0.1197	65.16	5.77
2	0.2263	0.5404	0.1197	65.12	5.92
	2nd crop of crystals.				
3	0.2107	0.5013	0.1089	64.89	5.79
4	0.2161	0.5142	0.1072	64.89	5.55
5	0.2182	0.5205	0.1153	65.04	5.91
Calc. for $C_{30}H_{28}O_9.C_2H_4O_2$:				64.84	5.45
Calc. for $C_{30}H_{30}O_9.C_2H_4O_2$:				64.62	5.77

[1] *Loc. cit.*

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Analyses of other pure preparations of gossypol "acetate."

	Subst.	CO_2.	H_2O.	% C.	% H.
1	0.1943	0.4628	0.0963	64.94	5.55
2	0.2207	0.5257	0.1080	64.97	5.48
3	0.2022	0.4819	0.0989	64.98	5.47

Pure "free" gossypol, prepared from the gossypol "acetate" (recrystallized 4 times) by removal of acetic acid and crystallization from diluted alcohol.

1	0.2246	0.5573	0.1097	67.67	5.47
2	0.2381	0.5929	0.1165	67.90	5.48
3	0.2361	0.5861	0.1167	67.70	5.53

Free gossypol, earlier preparations, possibly less pure.

1	0.1953	0.4878	0.0969	68.11	5.55
2	0.2079	0.5183	0.1032	67.98	5.55
Calc. for $C_{30}H_{28}O_9$:				67.64	5.30
Calc. for $C_{30}H_{30}O_9$:				67.39	5.66

Compound of Gossypol with Acetone.

4.09 g. of pure gossypol was dissolved in ether and the ether removed by adding warm water. The crusts of gossypol left were redissolved in ether and the process repeated. The aqueous filtrate in each case was titrated separately with 0.1 *N* sodium hydroxide. The first filtrate required 68.8 cc. and the second 1.2 cc. of alkali to neutralize. The total—70.0 cc.—is equivalent to 10.27% acetic acid in the gossypol "acetate" used. The wet crusts were then dissolved in acetone and the solution concentrated. Beautiful glistening crystals separated, which were filtered out, washed with diluted acetone and dried in an exhausted desiccator. The analyses for carbon and hydrogen showed the substance was not identical with free gossypol. A weighed portion of the substance heated to 140–150° lost 1.0% in weight. Heated further to 200° it lost 16.24%. It thus differed from free gossypol, which loses about 7% in weight at 200°, and from gossypol "acetate" which loses 16.5–16.6% at this temperature. The vapors from heating the gossypol crystallized from acetone were passed through water which was found to give a positive result with Rothera's test for acetone. The substance is then a compound of gossypol with acetone.

Analysis of gossypol "acetonate."

Subst. 0.1532, 0.2240; CO_2, 0.3787, 0.5540; H_2O, 0.0808, 0.1181.

Calc. for $C_{30}H_{28}O_9.CH_3COCH_3$: C, 67.11; H, 5.81. Found: C, 67.41, 67.45; H, 5.77, 5.90.

Acetyl and Benzoyl Derivatives.

The acetyl and benzoyl derivatives of gossypol were made several times, but all attempts to obtain crystalline products failed. The acetylated products usually had a pale yellow tinge, although one product obtained in small amount from diluted alcohol was completely colorless. Gossypol is not quickly acetylated by acetic anhydride alone, but the addition of

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a drop of pyridine, or sulfuric acid or some fused sodium acetate causes the reaction to proceed very rapidly.

Benzoyl gossypol is readily made by the Schotten-Baumann reaction. The reaction product is rather difficultly purified. It was obtained as a whitish amorphous powder which was easily saponified, like the acetyl compound, with alkali or strong sulfuric acid.

The acetyl and benzoyl compounds were analyzed for carbon and hydrogen. The data for the particular acetyl derivative analyzed agree well for a tetra-acetyl gossypol. There is some evidence that more than 4 hydroxyls may be present for the results of the methods of determining the number of acetyl groups by direct weighing of the reaction product, and by hydrolysis of the acetyl derivative with strong sulfuric acid and subsequent weighing of the gossypol set free, indicate the probable presence of 5 hydroxyls.

The benzoyl compound gave results with the acid hydrolysis indicating 5 benzoyl groups, but the analyses for carbon and hydrogen agreed better for a lower benzoate. It is quite possible that some unexplained change may occur in the sensitive gossypol on acetylation or benzoylation.

Analyses of acetyl gossypol made, using pyridine as accelerator.

	Subst.	CO_2.	H_2O.	% C.	% H.
1	0.1648	0.3935	0.0806	65.13	5.48
2	0.1636	0.3912	0.0826	65.21	5.65
3	0.1655	0.3946	0.0822	65.03	5.56
Calc. for $C_{30}H_{24}O_5.(OCOCH_3)_4$:				65.11	5.18
Calc. for $C_{30}H_{26}O_5.(OCOCH_3)_4$:				64.93	5.45

Benzoyl gossypol made by Schotten-Baumann method.

1	0.1925	0.5126	0.0864	72.63	5.02
2	0.1320	0.3502	0.0593	72.35	5.03
Calc. for $C_{30}H_{24}O_5(OCOC_6H_5)_4$:				73.28	4.68

As the acetyl gossypol, like gossypol, is insoluble in water, it seemed possible to estimate the number of acetyl groups in the substance by simply weighing up the product precipitated in amorphous flocks from the acetylation mixture. In one case the pyridine method gave a product which weighed 41% more than the original gossypol after 8 hours' drying in the steam oven. A second experiment was conducted using 1.103 g. portions of gossypol "acetate" equal to exactly 1 g. of gossypol. One portion was dissolved in 10 cc. acetic anhydride and boiled for a few minutes after the addition of one drop of pyridine. The other portion was acetylated by boiling with 20 cc. of anhydride and 2 g. of fused sodium acetate. The excess anhydride was destroyed with alcohol and the acetylated products precipitated with water and collected, dried, and weighed from time to time. It was found impossible to bring the substances to constant weight for they continued to lose weight at the temperature of the water oven. The weights after the first and after the eighth drying are given below:

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	(1) Pyridine—% increase.		(2) Sodium acetate—% increase.	
1st drying.....	1.3467	34.67	1.4288	42.88
8th drying.....	1.1965	19.65	1.2133	21.33

Calc. for $C_{30}H_{24}O_5(OCOCH_3)_4$: % increase in weight, 31.6%; calc. for $C_{30}H_{22}O_4(OCOCH_3)_5$: % increase in weight, 39.5%; calc. for $C_{30}H_{22}O_3(OCOCH_3)_6$: % increase in weight, 47.4%.

This loss of weight on prolonged drying at the temperature of the steam bath vitiates the accuracy of this method. The substance apparently is not stable at this temperature.

Analyses of the benzoyl and acetyl derivatives were made by dissolving them in concentrated sulfuric acid, warming slightly and allowing to stand overnight. The acid was then diluted with water to precipitate the gossypol. This was then collected in tared crucibles.

Percentage of gossypol found in acetyl gossypol.

1.... Subst., 0.2582 g. gave 0.1850 g. gossypol.....	= 71.6%
2.... Subst., 0.1204 g. gave 0.0847 g. gossypol.....	= 70.3%
Calc. for $C_{30}H_{24}O_5(OCOCH_3)_4$.....	= 76.0%
Calc. for $C_{30}H_{22}O_4(OCOCH_3)_5$.....	= 71.7%
Calc. for $C_{30}H_{22}O_3(OCOCH_3)_6$.....	= 66.6%

Percentage of gossypol found in benzoyl gossypol.

1.... Subst., 0.0823 g. gave 0.0409 g. gossypol.....	= 49.7%
2.... Subst., 0.0822 g. gave 0.0421 g. gossypol.....	= 51.2%
Calc. for $C_{30}H_{24}O_5(OCOC_6H_5)_4$.....	= 56.2%
Calc. for $C_{30}H_{22}O_4(OCOC_6H_5)_5$.....	= 50.6%

Using a special modification of the method of Verley and Bolsing[1] for the determination of acetyl groups, it was found that, on *short* boiling in the presence of pyridine, gossypol apparently gives a tetra-acetyl derivative. The results corresponded to a 29.6% increase in weight due to addition of acetyl instead of 31.6% calculated for 4 acetyl, or 39.5% for 5 acetyl groups added. The reaction proceeds so smoothly that it was assumed, perhaps incorrectly that the gossypol is thus completely acetylated. The evidence is sufficient, however, to show there are 4 or 5 hydroxyl groups in gossypol.

Salts of Gossypol.

Gossypol readily forms salts with alkalies. It dissolves easily in aqueous sodium hydroxide, carbonate and very slowly in bicarbonate and disodium phosphate. Gossypol may be titrated as a dibasic acid with dilute alkali using phenolphthalein as an indicator. The alkali salts are very soluble in water and alcohol and are extremely sensitive to oxidizing agents. The yellow color of their solution soon turns greenish brown and then slowly to a beautiful blue which in turn gradually disappears. The alkali salts may be precipitated by saturated salt solution and a similar salting out action of the alkali is noted when attempts are made to break up gossypol with fused alkali.

[1] *Ber.*, **34**, 3354, 3359 (1901).

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Lime water and baryta water do not dissolve gossypol as readily as do alkali hydroxides, which seems to be due to the lesser solubility of these salts. Neutral salts of the alkaline earths do not precipitate gossypol from its alcoholic solutions, neither do silver mercury or copper salts. Iron sulfate and lead acetate give amorphous brownish and yellow lake-like precipitates, respectively, from alcoholic solutions of gossypol. Gossypol does not readily dissolve in strong or dilute ammonia water. The ammonium salt is probably formed but as an insoluble compound. After warming gossypol with dilute ammonia and cooling, the liquid formed a gelatinous mass, evidently due to the physical properties of the ammonium salt.

Compound of Gossypol with Aniline.

Gossypol dissolves readily in warm aniline with which it combines to form a bright orange-yellow substance,[1] which is possibly the dianiline salt of gossypol which separates out almost quantitatively on cooling the solvent. It is possible that instead of being a simple aniline salt of gossypol it may be a condensation product of carbonyl groups in gossypol with the amino group of aniline. The substance dissolves in alcoholic potash with a blood-red color which seems to persist for a period longer than one would expect if the alkali immediately replaced the aniline at the acid groups. Both "B" gossypol and "D" gossypol, described later, give similar orange-yellow precipitates.

The insolubility of the aniline compound of gossypol furnishes a method of determining the amount of gossypol in cottonseed products, and therefore a chemical method for determining the relative toxicity of a cottonseed product. These compounds do not dissolve readily in the usual organic solvents but are least soluble in petroleum solvents. Warm aniline dissolves them readily and they separate out in crystalline form on cooling. Alcoholic potash dissolves them with a beautiful red color which, however, disappears after the compound is decomposed by the reagent into gossypol and aniline.

The aniline compound of gossypol was first made by Dr. J. T. Dobbins

[1] This substance heated to 100° was found to contain 3.97% nitrogen, which agreed sufficiently well with the 3.90% required for a substance of the formula $C_{30}H_{28}O_8 \cdot 2C_6H_5NH_2$. This seemed at the time to be the most plausible explanation of the reaction since gossypol behaves as a fairly strong dibasic acid. Later this analysis was checked by another chemist, who reported 4.35 and 4.38% nitrogen on the unheated material. This appeared to indicate that aniline was disengaged on heating. I have more recently made analyses of this same preparation and have found 4.61, 4.64, 4.84, 4.70% nitrogen in the unheated substance. There is no perceptible odor of aniline to this substance. The average of 4.65% for the three most closely agreeing results agrees better for a compound containing 2 molecules of gossypol to 5 molecules of aniline, $2C_{30}H_{28}O_8 \cdot 5C_6H_5NH_2$, which requires 4.58% nitrogen. My analyses of the aniline compounds "B" gossypol and "D" gossypol show, respectively, 4.84% and 4.15% nitrogen.

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in this laboratory. It was desired to see if "B" gossypol, which at that time was thought to be the product in cottonseed meal formed from gossypol in the cooking process, could be made without the formation of the black material which accompanies it when gossypol is heated to 180–190°. It was thought by Dr. Dobbins that by heating the gossypol in aniline this could be avoided. It was found, however, that even in boiling aniline the gossypol was not decomposed as in dry heating. On cooling the solvent it was noticed that an orange-yellow crystalline substance was deposited. This interesting compound is not appreciably toxic, probably on account of its extreme insolubility. It passes through the digestive tract unchanged.

New Compounds of Unknown Formulas Derived from Gossypol.

Three substances which resemble gossypol more or less have been isolated. Two of these are yellow. The third was not isolated in a pure form but appeared to be without color. By heating of gossypol in air to its decomposition point a substance called for convenience "B" gossypol is formed, together with a black resinous substance. "C" gossypol is without color and is formed by fusing gossypol with alkalies to a fairly high temperature. "D" gossypol is the name given to a product isolated from cottonseed meal and which is thought to be the substance formed from gossypol in the cooking of the cottonseed. These three substances resemble gossypol in that they dissolve in strong sulfuric acid with the blood-red color characteristic of gossypol, and also oxidize in alkaline solution with the production of the beautiful blue color formed by gossypol.

Preparation of "B" Gossypol.—On heating gossypol or gossypol "acetate" to the decomposition point, 186–190°, these substances fuse with the evolution of vapor and then the melt solidifies to a black mass. This mass loses no more weight on heating to 220°. The loss in weight in case of dry free gossypol is about 6.5% and about 16.5% for the "acetate." This corresponds to a loss of two molecules of water from gossypol and two molecules of water and one molecule of acetic acid from the "acetate." If the melt is treated with limited amounts of ether, the black resinous matter passes into solution and a sparingly soluble yellow substance crystallizes out. This substance is more intensely yellow than gossypol and melts around 246–248°. It is much less toxic than gossypol. It is acidic like gossypol and has a neutralization value of about 300.

Preparation of "C" Gossypol.—In attempts to split gossypol into simpler known substances it was fused with alkali. In the concentrated alkali gossypol forms a yellow salt which is apparently salted out so that it does not mix readily with the melt. In one experiment the melt was heated more strongly than usual. It was dissolved in water, with the addition of a pinch of sodium hyposulfite to prevent oxidation. On acidifying a *white* flocculent precipitate formed instead of the usual yellow one.

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The white precipitate was removed from the liquid with ether. The ether was evaporated to small volume and a little glacial acetic acid added. The new substance appeared to be very sensitive to oxidation for the solution rapidly became dark on standing. After some time a few crystals were formed. These appeared to be crystals of a colorless substance stained with brownish impurities. The substance dissolves in alkalies with an almost instantaneous formation of the blue color. On close examination, however, it was noted that this was preceded by a transient yellow-brown color. It is possible that the substance is closely related to the purple oxidation product of gossypol.

Preparation of "D" Gossypol.—The isolation of a gossypol-like substance from cottonseed *meal* furnishes an answer to the question of what becomes of gossypol in the cooking of cottonseed. Although gossypol may be easily removed from raw seed by ether, the same method applied to the meal failed to give an extract containing more than a trace of gossypol. The ether-extracted meal, however, gave a color reaction with alcoholic potash indicating the presence of much gossypol or a similar substance. It was earlier assumed that this was due to gossypol held perhaps dye-like by the seed tissue. The fact that gossypol combines with acetic acid and with aniline to form less soluble compounds suggested the idea that perhaps it was chemically combined with either carboxyl or amino groups of the protein. But the very slight toxicity for rats of cooked seed as compared with raw seed led to the conclusion that very little, if any, unchanged gossypol could exist in the cooked product. All attempts however to isolate this substance in the meal failed until it occurred to the writer to employ aniline as a solvent. It appears that under the influence of proper cooking conditions, conducted for a sufficient time all the toxic gossypol of the raw seed is changed to a substance which in the *meal* is so slightly toxic that on certain resistant species like the rat and fowl it has little or no effect if the diet is otherwise adequate.

The presence of this substance in considerable amounts in cottonseed *meal* accounts for the failure to find little or no gossypol-like substance in crude cottonseed oil (hot pressed) or in the ether extract of cottonseed meal.

To prepare "D" gossypol the cottonseed meal either before or after ether extraction is warmed to about 110° with enough aniline to make a thin paste. The meal turns to a deep brownish color. The aniline is sucked off on a Büchner funnel as much as possible, and the residue is washed with small amounts of ether until the filtrate is nearly colorless. The ether is driven off and the aniline solution allowed to stand for several days. A deposit of orange-yellow crystals appears after a day or so and gradually increases. The crystals obtained are often beautiful prisms over a millimeter long. This substance is the aniline compound of "D" gossypol. "D" gossypol was prepared from it by dissolving the substance in

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alcoholic potash and pouring into water. Oxidation was prevented by adding a pinch of sodium hyposulfite. The "D" gossypol was then precipitated in amorphous flocks by adding acid. The precipitate was taken up with ether. After evaporation of most of the ether, alcohol was added and the evaporation continued until a substance began to separate, after which a little more alcohol was added and the warm mixture allowed to cool. A crop of yellow crystals was secured. The substance showed no well-defined melting point but darkened and softened around 256°.

Unfortunately the author was not able to do more work on this substance. The method for obtaining it was worked out just before he left the experiment station. Certainly more work should be done on this substance, which occurs to such a considerable extent in cottonseed meal.

From a 100 g. sample of a meal cooked 28 minutes the aniline extraction, after previous ether extraction, gave 1.2 g. of the aniline salt of "D" gossypol. About one g. of the aniline compound was obtained from 100 g. of a meal which had been cooked 2 hours. Qualitative tests on cottonseed flour also showed a considerable amount present.

Since the food-products examined were definitely injurious to rabbits and pigs and since no gossypol *as such* could be found in these products, these facts indicate that this "D" gossypol gives rise to cottonseed-meal poisoning of rabbits and swine. The substance has so little action on rats that it is not possible to state whether the animals are affected by an active substance or are suffering from nutritive deficiencies. There are then chemical reasons for believing that cottonseed meal poisoning of swine may be due to the presence of unchanged gossypol, or to "D" gossypol, or to the presence of both.

Action of Nitric Acid on Gossypol.

Strong nitric acid dissolves gossypol with evolution of nitric peroxide fumes and with formation of a substance no longer giving the color reactions of gossypol. The product is soluble in alkalies with a reddish yellow color and is precipitated by acids. It could not be obtained in crystalline form.

Oxidation of Gossypol in Alkaline Solution.

Alkaline solutions of gossypol oxidize readily on exposure to air or more readily by adding hydrogen peroxide. This oxidation proceeds in several stages. A blue substance is formed first which may be reduced by alkaline hyposulfite to the yellow gossypol. The blue stage subsequently disappears and a more stable oxidation product is obtained which has little coloring power. This substance can not again be reduced to gossypol. It is precipitated by acids and dissolves in alkalies. Many attempts to obtain it crystalline were without success. The substance seemed to be rather complex. It resembled gossypol in its solubility in the solvents.

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Chemical Constitution.

Attempts to get a clue to the constitution of gossypol have failed through inability to split the substance into simpler known substances.

The fact that several flavone pigments occur in the cotton plant and the fact that gossypol has 30 carbon atoms suggests that it may be derived by condensation and subsequent reduction of two molecules of a flavone. The acidic properties are thought to be due to carbonyl and hydroxyl group arranged as in flavonols rather than to carboxyl groups. These substances are sufficiently acid to form salts from an alkali acetate. The presence of *o*-hydroxyl is indicated by the green ferric chloride reaction and by the formation of lake-like compounds with lead and ferrous salts. The presence of 9 oxygen atoms may be readily accounted for by the presence of 5 hydroxyls, 2 carbonyl groups and 2 bridge oxygen atoms, all of which types occur in the flavonols.

Presence of Gossypol as such in Commercial Cottonseed Products.

Examination of a number of cottonseed products with a view to determining the fate of gossypol has given results which are of considerable interest. Very little, if any, gossypol was found in samples of hot pressed meal. In one case a small amount was found where the seed used was very dry. On the other hand in the so-called "cold pressing" process at least three-fourths of the gossypol of the seed passed into the oil. Such an oil was found to contain 1.5% gossypol. On treatment with alkali any gossypol in the crude oil is quantitatively removed and passes into the foots. Since crude oil is always treated with alkali no gossypol or related pigment is ever found in the refined edible oil. Since the non-occurrence of gossypol in hot pressed oil is contrary to what might be expected and since it does not occur in *actually cold pressed* oil it may be well to explain the difference. Actual cold pressure squeezes out the oil from the oil cells without allowing it to dissolve gossypol from the "resin glands." Hence the gossypol remains in the press cake. In the commercial "cold pressing" process the seed is heated to a considerable extent and the material is subjected to a grinding, pulverizing action under great pressure so that the glands are broken up and the contents taken up by the hot oil and removed mostly from the cake.

In the hot pressing process as ordinarily conducted under the moist cooking conditions the gossypol glands are disintegrated by the moisture and stirring and the contents stream out and are spread over the seed tissue, where the gossypol is subjected to oxidizing influences. It is not clear why so little passes into the oil, but perhaps the seed tissue holds the gossypol and its oxidation product—"D" gossypol— much as cloth holds a dye, or possibly some chemical combination may take place.

If rather dry seed is used the gossypol is apparently not so readily converted to this less soluble, less toxic oxidation product but remains in

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part as such in the meal. Such a meal is more toxic than a properly cooked meal. In these cases gossypol may be extracted with ether and the amount estimated by the aniline method. It is interesting to note that gossypol in crude oil behaves much the same as free fatty acid. This was shown by dissolving some gossypol in neutral cotton oil, after which alkali was required to render the oil again neutral to phenolphthalein.

Thus the presence of a considerable amount of gossypol in crude oil would increase the refining loss. The writer has been informed that commercial "cold pressed" oil tends to show a smaller refining loss than hot pressed oil. Provided the same seed were used in each process the author believes that the reverse would be true owing to the presence of considerable amounts of gossypol in the crude cold-pressed oil.

West Raleigh, N. C.

[Contribution from the Laboratories of Bacteriology, University of Illinois.]

STUDIES ON THE BACTERIAL METABOLISM OF SULFUR.

II. FORMATION OF HYDROGEN SULFIDE FROM CERTAIN SULFUR COMPOUNDS BY YEAST-LIKE FUNGI.

By Fred W. Tanner.

Received January 15, 1918.

In a series of studies which are being made on the relation of sulfur to bacterial metabolism, it seemed important to investigate this question with regard to the yeasts. Even though these microörganisms are not bacteria, the report of this investigation is included in the series. In a former paper, the author[1] has shown that bacteria are important in forcing sulfur through its cycle. Little data are available in the literature with regard to the relation of sulfur compounds to the metabolism of yeasts. A great part of that which does exist must be taken from reports of investigations which are directly concerned with other things. Lafar[2] who has given a fairly complete résumé of the work on sulfur has stated that the sulfur metabolism of yeasts is very much in the dark.

Small amounts of sulfur are probably necessary in the nutrition of the budding fungi. Ash analyses of yeasts made by different investigators are reported by Lafar[2] which show a variation in sulfur trioxide content of from 0 to 6.38 per cent. Since sulfur has been found in most yeasts, it seems reasonable to assume that it may be closely connected with their metabolism.

De Rey-Pailhade[3] reported the formation of hydrogen sulfide by yeasts and believed that its formation was due to the reducing enzyme which he called *philothion*. These data were later verified by Sostegni and San-

[1] Tanner, F. W., *Jour. Bact.*, **2**, 585–593 (1917).

[2] Lafar, F., *Handbuch der Technischen Mykologie*, **4**, 83–84 (1904).

[3] De Rey-Pailhade, M. J., *Bull. soc. chim.*, [3] **23**, 666–668 (1900).

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nino.[1] To prove this, a pure culture of yeast was inoculated into a sugar solution containing sulfur. The evolution of hydrogen sulfide was soon observed. Pozzi-Escot[2] stated that *philothion* could also reduce selenium and phosphorous compounds and possibly arsenic and tellurium salts. Euler[3] does not agree with de Rey-Pailhade nor Pozzi-Escot that *philothion* is a reducing enzyme. It is now known under the name of *hydrogenase* (Grüsse;[4] de Rey-Pailhade[5]). That hydrogen sulfide is given off from certain industrial fermentations has been known for a long time.

Experimental.

The strains of yeasts which were used in this investigation came from different sources. The most of them, however, were received through the kindness of Doctor H. W. Anderson[6] who has recently published an extended study of the yeast-like fungi. No sharp line may be drawn between the different groups of fungi and in this paper some are included which might not be regarded as yeasts.

The technique of the investigation was quite similar to that described in a former paper. Strips of bibulous paper which had been treated with a saturated solution of lead acetate to which a small amount of glycerol had been added, were suspended in test tubes over the sulfur-containing substrate. The medium which was used had the following composition:

Triple distilled water	1000 cc.
Asparagin	2 g.
Dibasic sodium phosphate	1 g.
Dextrose	50 g.
Ammonium chloride	Trace
Ferric chloride	Trace
Magnesium chloride	Trace

This medium amply supplied the requirements of the yeasts, and all of them grew vigorously after the sulfur-containing compound had been added. Several control tubes were incubated which checked the chemicals used in the special medium and showed that the hydrogen sulfide which was observed, came from the special sulfur compound upon which the action of the yeast was being studied. Inoculations were made from dextrose agar slants, great care being taken to prevent taking any of this medium over to the culture tubes. Since the yeasts grew abundantly with a distinctly raised growth, this was accomplished with no difficulty. The culture tubes were incubated for 30 days at room temperature which

[1] Sostegni, L., and Sannino, A., *Chem. Centr.*, **61**, 2, 112 (1890).

[2] Pozzi-Escot, M. E., *Bull. soc. chim.*, [3] **27**, 280 (1902).

[3] Euler, H., "General Chemistry of the Enzymes," Trans. Pope, John Wiley & Sons, New York, 1912.

[4] Grüsse, J., *Woch. Brau.*, **27** (1903). Original not seen. Quoted by Guilliermond in Les Levures, Paris, 1912.

[5] *Loc. cit.*

[6] Anderson, H. W., *J. Infect. Dis.*, **21**, 341–386 (1917).

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varied from 24° to 30°. A summary of the results which were secured with the various compounds is given in Table I wherein the extent of hydrogen sulfide formation is roughly expressed.

Peptone.—A three per cent. solution of Witte's peptone in the special medium was used. Vigorous growth was observed in all cases but not all of the yeasts liberated hydrogen sulfide from peptone. Eleven of the 30 pure cultures of yeasts formed it, with *Mycoderma lactis* forming the largest amounts. With the bacteria as reported in a former paper it was found that a few reduced the sulfur in peptone but not that in cystine to hydrogen sulfide. This was not observed with the fungi which form the basis of this investigation. Fearing that the dextrose in the medium might be inhibiting the decomposition of the peptone a portion of the special medium was prepared without the addition of the dextrose. This was inoculated with those strains which formed no hydrogen sulfide from the original medium. Under these conditions *Saccharomyces ellipsoideus* Hansen and *Torula monosa* formed hydrogen sulfide.

Cystine.—This was prepared directly from wool according to Folin's[1] method. In order to conserve the supply of this compound, a 2% solution was distributed into small test tubes. Not over 4 cc. were used in any of the culture tubes. All of the strains of fungi used in this investigation reduced the sulfur in cystine to hydrogen sulfide. Some of these formed no hydrogen sulfide from peptone according to the method used in this investigation. The detailed results for each strain may be obtained from Table I.

Sodium Taurocholate.—A 2% solution of Merck's sodium taurocholate was used. This yielded a medium in which there was vigorous growth. *Oidium albicans* and *Mycoderma lactis* were the only strains which gave unmistakable evidence of hydrogen sulfide formation from this compound.

Sodium Phenolsulfonate.—A 3% solution of this compound in the special medium was used. None of the strains used in this investigation attacked the sulfur linkage in sodium phenolsulfonate. All of them grew well, many of them showing the characteristic growth of top yeasts.

Sodium Sulfate.—A 3% solution of this compound in the special medium was used. Beijerinck,[2] has stated that yeasts are unable to reduce sulfates to hydrogen sulfide. Kossowicz and Loew[3] reported an investigation which confirmed the statements of Beijerinck. Among the strains of yeast which they used and which were used in this investigation were *Saccharomyces cerevisiae* and *Saccharomyces ellipsoideus*.

In this investigation, 9 of the 30 pure cultures of yeast-like fungi formed

[1] Folin, O., *J. Biol. Chem.*, 8, 9–10 (1910).
[2] Beijerinck, M. W., *Centr. Bakt. Parasitenk., II Abt.*, 6, 194–206 (1900).
[3] Kossowicz, A. L., and Loew, W., *Z. Gärungsphysiol.*, 2, 87–103 (1912).

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TABLE I.—HYDROGEN SULFIDE FORMATION BY YEASTS.

Name of fungus	Peptone.	Cystin.	Sodium thio-sulfate.	Sodium sulfate.	Sodium sulfite.	Potassium sulfo-cyanate.	Thio-urea.	Sodium phenol sulfon.	Sodium tauro-cholate.	Sulfur.
Saccharomyces marxianus	—	+	—	—	+	—	+	—	—	+
Saccharomyces ellipsoideus Hansen	—	1+	4+	—	+	—	—	—	—	+
Saccharomyces hominis Busse	—	+	—	—	—	—	—	—	—	—
Saccharomyces anomolous Hansen	1+	2+	+	+	+	+	—	—	—	2+
Saccharomyces anomolous Hansen	1+	2+	4+	+	+	+	—	—	—	+
Saccharomyces albus	—	+	2+	—	+	—	2+	—	—	—
Saccharomyces glutinis (Fres) Cohn	—	+	1+	—	+	—	—	—	—	—
Zygosaccharomyces bisporus Anderson	—	+	2+	—	+	—	—	—	—	1+
Saccharomyces of Cutris	—	+	1+	+	+	—	—	—	—	+
Parasaccharomyces Thomasii Anderson	—	+	4+	—	+	—	—	—	—	4+
Parasaccharomyces Ashfordii Anderson	—	+	3+	—	+	+	1+	—	—	—
Willia belgica Lindner	+	+	—	—	+	—	—	—	—	+
Mycoderma monosa Anderson	+	3+	4+	1+	5+	3+	—	—	—	4+
Mycoderma vini	+	3+	4+	1+	5+	3+	2+	—	—	—
Pseudosaccharomyces Stevensii Anderson	+	+	1+	—	—	—	—	—	—	1+
Monilia candida **Bon**	+	1+	4+	+	+	2+	3+	—	—	1+
Schizosaccharomyces Pombe **Lindner**	—	+	2+	—	+	—	—	—	—	1+
Cryptococcus glabratus Anderson	+	+	—	—	+	—	—	—	—	1+
Cryptococcus verrucosus Anderson	—	+	—	—	+	—	—	—	—	+
Oidium albicans **Ch. Robin**	—	+	3+	—	+	—	2+	—	+	1+
Mycoderma lactis	2+	1+	4+	1+	3+	3+	+	+	+	+
Torula humicola **Daczewska**	—	—	—	—		—	—	—	—	—
Saccharomyces **of Binot**	—	+	3+	—	+	—	+	—	—	+
Champagne yeast	—	+	—	+	+	—	+	—	—	+
Burgundy wine yeast	—	1+	4+	1+	+	—	+	—	—	+
Brewers' yeast	1+	4+	—	—	+	3+	—	—	—	1+
Saccharomyces cerevisiae **Hansen**	—	+	1+	—	—	—	+	—	—	—
Cryptococcus agregatus **Anderson**	—	+	1+	—	—	+	+	—	—	+
Torula monosa	—	+	2+	—	—	—	—	—	—	—
Torula datilla	+	1+	—	+	—	—	+	—	—	+

+ = edge of the lead acetate paper darkened.
1+ = about 1 cm. of the paper darkened.
2+ = about 2 cm. of the paper darkened.
3+ = etc.
4+ = etc.

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hydrogen sulfide from sodium sulfate. None of these strains were among those used by Kossowicz and Loew. This may possibly explain their statement that yeasts do not reduce sulfates to hydrogen sulfide. Had they used more than four strains, it is possible that they would have observed hydrogen sulfide formation from some of them.

Sodium Sulfite.—A 3% solution of sodium sulfite was used. Twenty-three of the strains reduced the sulfur in sodium sulfite to hydrogen sulfide. In this compound, the sulfur is partly reduced, which may explain why a greater number of the yeasts produced hydrogen sulfide from sodium sulfite than from sodium sulfate. The bacteria are not able to reduce sulfates under aerobic conditions but could reduce the less highly oxidized forms of sulfur. Also, the yeasts seem to be less sensitive to sulfites than the bacteria. Nagaeli[1] has stated that sulfates, hyposulfites and sulfites may serve as sources of sulfur for yeasts.

Sodium Thiosulfate.—Beijerinck[2] found that yeasts could form hydrogen sulfide from thiosulfates. Hahn (1903) showed that the juice pressed from yeasts cells exhibited a reducing action on sulfur. Kossowicz and Loew[2] extended our knowledge on this subject by asserting from data which they present, that yeasts are able to use thiosulfate sulfur in their metabolism. No free sulfur nor sulfates could be detected by these investigators in their culture flasks. To study this question more extensively the following work was carried out:

A 3% solution of Merck's sodium thiosulfate in the special medium was used. In this the control culture tubes showed the formation of hydrogen sulfide. This probably took place according to the following equations:

$$Na_2S_2O_3 + NaH_2PO_4 = H_2S_2O_3 + Na_3PO_4$$

$$H_2S_2O_3 + H_2O = H_2S + H_2SO_4$$

The use of the normal sodium phosphate reduced the amount of hydrogen sulfide formed spontaneously without the aid of the microörganisms but it was not used in any of the culture media. In no case did the blank tubes show as much darkening of the lead acetate paper as the culture tubes. In order to secure accurate data with regard to this compound, the contents of the culture tubes were precipitated with cadmium carbonate and filtered through a dry filter paper. Five cc. of the filtrate were then titrated with 0.1 *N* iodine solution. The results are shown in Table II and are calculated to the amount of thiosulfate which disappeared from 100 cc. of medium. Corrections were made by means of two blanks so that the loss there indicated was directly due to the action of the microorganisms.

[1] Nagaeli, see "Technical Mycology," by Franz, Lafar, trans. Salter. Vol. 2, Part I, p. 48. C. Griffen and Company, London, 1912.

[2] *Loc. cit.*

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TABLE II.—DECOMPOSITION OF SODIUM THIOSULFATE.

Culture No.	Name of fungus.	Mg. $Na_2S_2O_3$ decomposed in 100 cc. of medium.
1	*Saccharomyces marxianus*	0
2	*Saccharomyces ellipsoideus*	30.02
3	*Saccharomyces hominis*	0
4	*Saccharomyces anomolous*	23.70
5	*Saccharomyces anomolous*	26.22
6	*Saccharomyces albus*	14.85
7	*Saccharomyces glutinis*	11.06
8	*Zygosaccharomyces bisporus*	12.64
9	*Saccharomyces* of Curtis	12.64
10	*Parasaccharomyces Thomasii*	12.64
11	*Parasaccharomyces Ashfordii*	20.54
12	*Willia belgica*	0
13	*Mycoderma monosa*	31.60
14	*Mycoderma vini*	28.44
15	*Pseudosaccharomyces Stevensii*	11.48
16	*Monilia candida*	23.70
17	*Schizosaccharomyces Pombe*	12.64
18	*Cryptococcus glabratus*	0
19	*Cryptococcus verrucosus*	0
20	*Oidium albicans*	23.70
21	*Mycoderma lactis*	34.76
22	*Torula numicola*	0
23	*Saccharomyces* of Binot	23.70
24	Champagne yeast	0
25	Burgundy wine yeast	22.12
26	Brewers' yeast	0
27	*Saccharomyces cerevisiae*	11.48
28	*Cryptococcus agregatus*	12.08
29	*Torula monosa*	13.07
30	*Torula datilla*	0

Twenty-one of the pure strains of yeasts used in this investigation formed hydrogen sulfide from sodium thiosulfate. No sulfates nor free sulfur could be detected in the culture tubes. Sulfites were demonstrable. This is in accord with the work of Neuberg and Welde[1] who report that yeasts break up thiosulfate according to the following equation:

$$Na_2S_2O_3 + H_2 = H_2S + Na_2SO_3$$

and not according to the following

$$Na_2S_2O_3 + H_2O = NaSO_4 + H_2S$$

Potassium Thiocyanate.—Thirty g. of the pure salt were added to a liter of the special medium, in which all of the strains grew well. Gröller[2] studied the thiocyanates as sources of carbon, nitrogen and sulfur for bacteria yeasts and molds. Thiocyanates were utilized as sources of sulfur

[1] Neuberg, C., and Welde, E., *Biochem. Z.*, **67**, 111–118 (1915).

[2] Kossowicz, A., and Gröller, L., 1912–1913; *Z. Gärungsphysiol.*, **2**, 159–165 (1912).

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and nitrogen but not for carbon. Hydrogen sulfide was liberated in some cases but no free sulfur was produced.

Ten of the pure strains of yeasts attacked potassium thiocyanate with the liberation of hydrogen sulfide. *Mycoderma vini*, *Mycoderma monosa*, *Mycoderma lactis* and Brewers' yeast formed especially large amounts of hydrogen sulfide from this compound. Nagaeli has reported that ammonium thiocyanate was unsuitable as a source of sulfur for yeasts.

Thiourea.—A 3% solution was used. Fourteen of the yeasts formed hydrogen sulfide from it. Nagaeli has reported that this urea was unsuitable as a source of sulfur for yeasts.

Free Sulfur.—About 0.2 g. of Merck's resublimed sulfur was placed in the bottom of each culture tube, to which were added about 10 cc. of the special culture medium. After sterilization, this sulfur collected in the bottom of the culture tubes in the shape of a button but available for the yeasts. Eight of the strains formed no hydrogen sulfide from free sulfur. In each of these 8 tubes there was good evidence of vigorous growth.

Summary.

The budding fungi used in this investigation are able to reduce the sulfur in cystine to hydrogen sulfide. With regard to peptone this characteristic is less extensive. Most of the strains were able to attack the sulfur linkage in thiosulfate to produce hydrogen sulfide. Thiosulfates are probably reduced to sulfite and hydrogen sulfide. Contrary to statements in the literature that yeasts are unable to reduce sulfates, 10 of the strains used in this investigation reduced sodium sulfate to hydrogen sulfide. A few of the yeasts reduced sodium sulfite. Sodium taurocholate was reduced to hydrogen sulfide by 2 strains, while sodium phenolsulfonate was not, although there was good growth in this latter substrate. Potassium thiocyanate and thiourea were also reduced. Hydrogen sulfide was also formed by many of the yeasts from free sulfur. Yeasts seem to be able to split some of the more stable linkages of sulfur, a characteristic which is probably not so wide spread among the bacteria.

ANALOGUES OF ATROPINE AND HOMATROPINE.

By Louis F. Werner.

Received January 16, 1918.

The alkamine tropine, one of the hydrolysis products of atropine, is changed upon oxidation to the ketone tropinone. This ketone is closely related to another ketone known as pseudopelletierine, which occurs naturally in the bark of the pomegranate tree. The relationship between the two is shown by the following structural formulas:

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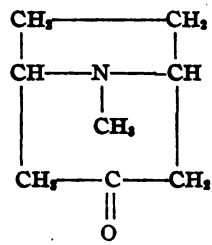
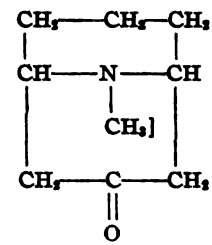


Tropinone.



Pseudopelletierine.

As can be readily seen, pseudopelletierine differs from tropinone in that it has one carbon atom and two hydrogen atoms more than tropinone.

Tropinone upon reduction is converted into two stereoisomeric alcohols. Upon being reduced electrolytically, or with concentrated hydriodic acid and zinc dust, it is reduced to tropine, but if reduced with sodium and alcohol it yields pseudotropine, a stereoisomer of tropine. These two stereoisomers have different physical properties, and the esters of these alcohols with the hydroxy acids have different physiological properties.

Pseudopelletierine upon reduction also gives two stereoisomeric compounds. Ciamician and Silber[1] found that an alkamine was formed upon reducing pseudopelletierine with alcohol and sodium, which they named methylgranatoline. The author found that a stereoisomer is formed by reducing pseudopelletierine with concentrated hydriodic acid and zinc dust, which may therefore be called iso-methylgranatoline. These two isomers have different physical properties, as is the case of the two reduction products of tropinone.

As was stated, an important difference in the properties of the reduction products of tropinone lies in the different physiological activities of the esters of the hydroxy acids with these alcohols. Thus the tropic acid ester (atropine), and the mandelic acid ester (homatropine) of tropine have strong mydriatic power, whereas the tropic acid esters and the mandelic acid ester of pseudotropine are devoid of such properties.

The object of the work undertaken was: To prepare the second reduction product of pseudopelletierine which was theoretically possible, and then to determine any difference in the physiological activities of the tropic acid and mandelic acid esters of these two stereoisomers.

The hydrobromides of the mandelic acid and tropic acid esters of isomethylgranotoline were prepared, and were found to have no mydriatic powers. These two artificial alkaloids were not obtainable in a crystalline condition, it being necessary to isolate them, and purify them in the form of their hydrobromides.

The hydrobromides of the mandelic acid and tropic acid esters of methylgranatoline were also prepared, and were found to have strong mydriatic

[1] *Ber.*, **26**, 2740 (1893).

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properties. The hydrobromide of the tropic acid ester was obtained as a crystalline powder, but the hydrobromide of the mandelic acid ester was obtained as a syrup only.

From the viewpoint of physiological activity alone, tropine and methylgranatoline should constitute one type of stereoisomer, that is the type whose hydroxy acid esters have mydriatic power, whereas pseudotropine and iso-methylgranatoline are another type of isomer whose hydroxy acid esters are lacking in mydriatic powers.

From the standpoint of physical properties we would predict different results from those found above, as we would naturally group tropine (m. p. 63°) and iso-methylgranatoline (m. p. 65°) together and pseudotropine (m. p. 108°) and methylgranatoline (m. p. 100°) together. From the analogy in the methods of preparation of tropine and iso-methylgranatoline, and of pseudotropine and methylgranatoline we would classify these compounds into these two groups also. Thus methylgranatoline is prepared by reducing pseudopelletierine with alcohol and sodium, and pseudotropine is prepared from the corresponding ketone tropinone in analogous manner: iso-methylgranatoline and tropine are both prepared from the corresponding ketones by reduction with zinc dust and hydriodic acid. These results show the uncertainty of associating similarity of chemical and physical properties of compounds with similarity in physiological behavior.

Experimental.

Preparation of Methylgranatoline.—The method used by Ciamician and Silber,[1] slightly modified, was followed. Ten g. of pseudopelletierine were dissolved in 200 cc. of ethyl alcohol, and metallic sodium added until no more would dissolve, the reaction being carried out in a flask heated by a metal bath. Water was then added, and the alcohol distilled off, and the aqueous alkaline residue made acid with hydrochloric acid. This acid solution was then saturated with sodium bicarbonate, and the unchanged pseudopelletierine removed by shaking out with chloroform. The solution was then made strongly alkaline with sodium hydroxide solution, and the methylgranatoline shaken out with chloroform. Upon drying the chloroform solution over anhydrous sodium sulfate, the methylgranatoline was obtained as a crystalline solid upon distilling off the chloroform. Upon recrystallizing from petroleum ether, the pure compound is secured, melting at 100° (uncorr.).

Preparation of Iso-Methylgranatoline.—The method used was analogous to that used by Willstaetter[2] in reducing topinone to tropine. Ten g. of pseudopelletierine were dissolved in 120 g. of conc. hydriodic acid (sp. gr., 1.96), and was then cooled to 0°. Twenty g. of zinc dust were then added,

[1] *Ber.*, **26**, 2740 (1893).
[2] *Ibid.*, **33**, 1174 (1900).

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stirring constantly, and the temperature was not allowed to rise above 0°. The reaction required about 2 hours. The mixture was allowed to stand for 24 hours, and then an excess of sodium hydroxide solution added, and the mixture shaken out with chloroform. This chloroform solution contained both pseudopelletierine and the new alcohol. In order to separate the two, the chloroform solution was shaken out with an excess of dil. hydrochloric acid, and after separating from the chloroform, the acid solution was saturated with sodium bicarbonate. This solution was then shaken out with chloroform to remove the pseudopelletierine, and then made strongly alkaline with sodium hydroxide solution, and the iso-methylgranatoline shaken out with chloroform. After being dried over anhydrous sodium sulfate, the alkamine is obtained as a crystalline residue upon removing the chloroform. It was then recrystallized from petroleum ether. The base is readily soluble in water, alcohol, and chloroform, but less soluble in petroleum ether. M. p. 65° (uncorr.).

Subst., 0.2515; N, 20.45 cc. at 761 mm. and 21°; collected over 30% KOH solution.

Calc. for $C_9H_{17}NO$: N, 9.032%. Found: 9.310%.

Preparation of the Hydrobromide of Tropic Acid Ester of Iso-Methylgranatoline.—Three g. of iso-methylgranatoline and 3 g. of tropic acid were dissolved in 10% hydrochloric acid, and the mixture heated for 70 hours on a water bath, the acid being replaced from time to time as it evaporated. The mixture was then diluted with water, and the excess tropic acid removed by shaking out with ether. Ammonia in excess was then added to the aqueous solution, and the ester shaken out with a little chloroform. The chloroform solution was extracted then with dilute hydrobromic acid, avoiding an excess. This aqueous solution of the hydrobromide was evaporated to dryness in a vacuum desiccator over conc. sulfuric acid. The dry residue was then recrystallized from absolute ethyl alcohol. It was found necessary to repeat the recrystallization several times to completely remove all ammonium bromide. The product so obtained was a white crystalline powder, turning yellow upon prolonged exposure to the light. It is soluble in water or hot alcohol, less so in cold alcohol. M. p. 233° (uncorr.).

Subst., 0.3909; N, 13.20 cc. at 757 mm. and 26°; collected over 30% KOH solution.
Calc. for $C_{18}H_{26}NO_3Br$: N, 3.64%. Found: 3.76%.

Preparation of the Hydrobromide of the Mandelic Acid Ester of Iso-methylgranatoline.—Three g. of iso-methylgranatoline and 3 g. of mandelic acid were dissolved in 10% hydrochloric acid, and were heated for 70 hours in an evaporating dish upon a water bath. The hydrochloric acid which evaporated was replaced, from time to time, by the addition of new acid. Only sufficient acid was added to keep all the reacting products in solution. At the end of the time stated, the reaction mass was diluted with a little

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water, and the excess mandelic acid removed by shaking out with ether. The alkaloid was liberated by adding ammonia water in excess and was then taken up with a little chloroform. The hydrobromide was secured from this chloroform solution by shaking out with dil. hydrobromic acid, and evaporating the aqueous solution in a vacuum desiccator over sulfuric acid. The pure hydrobromide is secured by recrystallizing the crude salt from absolute alcohol. M. p. 229° (uncorr.). The salt is readily soluble in water or hot alcohol, slightly soluble in cold alcohol.

Subst., 0.4155; N, 14.50 cc. at 763 mm. and 25°; collected over 30% KOH solution.

Calc. for $C_{17}H_{24}NO_3Br$: N, 3.78%. Found: 3.93%.

Preparation of the Hydrobromide of the Tropic Acid Ester of Methylgranatoline.—Four g. of methylgranotoline and 4 g. of tropic acid were heated for 70 hours in an evaporating dish on a water bath with 0.25% hydrochloric acid. Sufficient acid was added from time to time, to keep all the reacting substances in solution. At the end of this time the mixture was acidified with conc. hydrochloric acid, and the unchanged tropic acid removed with ether. The aqueous solution was then made alkaline with ammonia water, and the base taken up with chloroform. The hydrobromide was formed by extracting the alkaloid from the chloroform by shaking out with dilute hydrobromic acid. Upon evaporating this aqueous solution in a vacuum desiccator over sulfuric acid, the crude hydrobromide was secured, which was purified by recrystallization from absolute alcohol. M. p. 220° (uncorr.). The salt is readily soluble in water and hot alcohol, slightly soluble in cold alcohol.

Subst., 0.4209; N, 14.10 cc. at 759 mm. and 20°; collected over 30% KOH solution.

Calc. for $C_{18}H_{26}NO_3Br$: N, 3.64%. Found: 3.84%.

Preparation of the Hydrobromide of the Mandelic Acid Ester of Methylgranatoline.—This compound was made by heating 4 g. of mandelic acid and 4 g. of methylgranatoline with 0.25% hydrochloric acid in sufficient quantity to keep all the reacting substances in solution. After heating for 70 hours, the mixture was acidified with hydrochloric acid, and excess mandelic acid removed by shaking out with ether. The aqueous solution was then made alkaline with ammonia water, and the ester shaken out with chloroform. The hydrobromide was secured as a viscous syrup upon extracting this chloroform solution with dil. hydrobromic acid, and evaporating *in vacuo* over sulfuric acid. The sulfate and the hydrochloride were also made, but these also were obtained as syrups only. No analysis was attempted of these viscous products.

Conclusion.

The results of the work show that, analogous to tropinone, pseudopelletierine gave two stereoisomers upon reduction. Similar to the two isomers

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secured by the reduction of tropinone, one of these isomers when converted to the tropic or mandelic acid ester had no mydriatic properties, whereas the tropic and mandelic acid esters of the other had strong mydriatic effects. Use of the physical properties and methods of formation of these isomers was shown to be unreliable as a method of predicting their probable physiological effects.

The author wishes to express his gratitude to the Cincinnati Board of Health, in whose laboratory he was given the opportunity to determine the physiological effects of these alkaloids.

CINCINNATI, OHIO.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF YALE UNIVERSITY.]

THE RELATIVE STABILITY OF HALOGEN SUBSTITUTED ALIPHATIC ACIDS IN WATER SOLUTION.

II. THE PROPIONIC ACID AND BUTYRIC ACID SERIES.

BY G. S. SIMPSON.

Received January 21, 1918.

In a recent paper from this laboratory[1] the relative stability of halogen substituted acetic acids as determined by the hydrolysis of their sodium salts was discussed. This article describes the result of a similar investigation of the stability of several halogen substituted acids in the propionic and butyric acid series.

Preparation of Materials.

The ethyl esters of α-bromobutyric acid and α-bromoisobutyric acid, which were in stock, were readily purified by distillation. All other acids or esters were prepared as described below.

α-Chloropropionic ester was made from lactic acid by the method of Loven.[2] Dried calcium lactate was allowed to react with phosphorous pentachloride and the α-chloropropionyl chloride obtained was added to absolute alcohol to form the ester. After purification the product boiled at 145–147°.

α-Bromopropionyl bromide was made by adding bromine to dry propionic acid in the presence of red phosphorus according to Zelinsky's[3] method. This was added to absolute alcohol to form α-bromopropionic ester which, after purification, boiled at 157–159°.

β-Iodopropionic acid was prepared by heating iodine and yellow phosphorus with an aqueous solution of glyceric acid, obtained by the oxidation of glycerine with fuming nitric acid and purification by means of its calcium salt. This method of purification of glyceric acid, suggested by

[1] Drushel and Simpson, THIS JOURNAL, 39, 2453 (1917).

[2] *J. prakt. Chem.*, [2] 29, 367 (1884).

[3] *Ber.*, 20, 2026 (1887).

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Drushel,[1] gives a crystalline product which is much more convenient to isolate and wash than the gelatinous lead salt. The iodopropionic acid was obtained as pearly white plates by recrystallization from hot water.

β-Bromopropionic acid was formed by adding an aqueous solution of β-iodopropionic acid to bromine and subsequent heating according to Richter.[2] The free iodine formed was filtered off and all excess of halogen was removed by pressing the product on a porous plate. It was purified by recrystallizing from petroleum ether giving pearly plates melting at 62°.

β-Chloropropionic acid has been made by different methods by several investigators but in each case a different melting point was recorded. DeBarr[3] and Richter[4] prepared it by the replacement of iodine of β-iodopropionic acid in aqueous solution with chlorine. The product was then distilled several times over mercury or silver. Such a procedure might easily give adipic acid according to this equation:

$$2ClCH_2 - CH_2COOH + 2Ag \longrightarrow (CH_2\text{-}CH_2COOH)_2 + 2AgCl$$

The acid prepared in this manner melted at 58–61° while all the other procedures gave products melting at 35.5° to 41°. As De Barr gave no analysis of his product it is difficult to determine the true value of his method. Since β-iodopropionic acid was the only material available at this time for the preparation of β-chloropropionic acid, the method described by Drushel[5] for preparing esters of β-chloropropionic acid was used. Fifty g. of β-iodopropionic acid were dissolved in 100 g. of chloroform. This solution, which was well cooled, was treated with chlorine in the dark until no more iodine trichloride separated out. This precipitate was filtered on asbestos and the filtrate was placed in a vacuum desiccator over caustic soda. After distilling off the chloroform the remainder of free halogen was removed by pressing the product on a porous plate. On recrystallization from petroleum ether 20 g. of white pearly crystals melting at 39° were obtained. This product thus melted well within the limits given by several investigators. On analysis the following figures were obtained:

Subst., 0.2160, 0.2320; AgCl, 0.2902, 0.3084.
Calc. for $C_3H_5O_2Cl$: Cl, 32.70. Found: 32.90, 33.25.

An attempt was made to prepare β-chloropropionitrile by the selective action of potassium cyanide on β-chloro-α-bromoethane, synthesized by the method of James,[6] but large amounts of vinyl chloride were produced due to the alkalinity of potassium cyanide.

[1] *Am. J. Sci.*, 39, 113 (1915).
[2] *Zeit. Chem.*, 1868, 461.
[3] *Am. Chem. J.*, 22, 336 (1899).
[4] *Loc. cit.*
[5] *Am. J. Sci.*, 34, 69 (1912).
[6] *J. prakt. Chem.*, [2] 26, 380 (1882).

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The α,α-dibromopropionic acid was made by Drushel's[1] modification of the method of Phillipi and Tollens.[2] Dry propionic acid was heated in a sealed tube with bromine and the tube opened to allow the escape of hydrobromic acid. An equal amount of bromine was again added and the heating continued. The product was freed from hydrobromic acid and free halogen by pressing on a porous plate and then was recrystallized from a small amount of water. The material melted at 61°.

The preparation of α,β-dibromopropionic acid required the use of allyl alcohol which was made by Koehler's[3] method. By allowing allyl alcohol and bromine to stand in two crystallizing dishes several days under a bell jar β,γ-dibromohydrine was formed as described by Munder and Tollen.[4] This product was steam-distilled and then oxidized to α,β-dibromopropionic acid by means of fuming nitric acid. The material after recrystallizing from water melted at 63°.

α,β-Dichloropropionic acid was similarly made from allyl alcohol by Tollen's[5] method. The β,γ-dichlorohydrine formed by passing chlorine into a cooled flask containing allyl alcohol was distilled in a vacuum and then oxidized by fuming nitric acid to α,β-dichloropropionic acid. It was purified by washing and recrystallizing from hot water, giving a product melting at 49°.

α-Chlorobutyric acid was obtained by the method of Freer.[6] Ethyl malonic ester was formed by the action of ethyl iodide on sodiomalonic ester. This was chlorinated by Gutzeit's[7] method. The chloroethyl malonic ester was converted to potassium ethyl chloromalonate by an alcoholic solution of potassium hydroxide and from this the free acid was obtained by means of dilute sulfuric acid. On distilling ethyl chloromalonic acid in a vacuum (15 mm.) at 101°, carbon dioxide was split off and α-chlorobutyric acid passed over, as described by Freer.[8]

β-Chlorobutyric acid was made by saturating an ethereal solution of crotonic acid with hydrochloric acid gas according to De Barr.[8] After removing the ether β-chlorobutyric acid was distilled in a vacuum (22 mm.) at 116°. The crotonic acid was made by the method of Komnenos,[9] by heating malonic acid, acetic acid and paraldehyde together on a steam bath. It was separated from methyl glutaric acid, formed at the same time by removing the portion distilling over between 170–210°. This was puri-

[1] *Loc. cit.*
[2] *Ann.*, **171**, 315 (1874).
[3] *Bull. soc. chim.*, [4] **13**, 1103 (1913).
[4] *Ann.*, **167**, 224 (1873).
[5] *Ibid.*, **156**, 247 (1869).
[6] *Ibid.*, **319**, 357 (1904).
[7] *Ibid.*, **209**, 232 (1881).
[8] *Loc. cit.*
[9] *Ann.*, **218**, 145 (1883).

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fied by repeated distillation and recrystallized from hot ligroin giving a product melting at 71–72°.

When the esters were available, the sodium salts of halogen substituted aliphatic acids were obtained by treatment with a strong solution of caustic soda as previously described.[1] By this method sodium α-bromoisobutyrate separated out at once since it is quite insoluble in alcohol. In all other cases concentration of the solutions in a vacuum and subsequent isolation of the sodium salts was found necessary.

In cases where the free halogen substituted aliphatic acids were available they were simply neutralized by a calculated amount of 0.1 N solution of caustic soda free from sodium carbonate. These solutions were then hydrolyzed as described below.

Hydrolysis of Sodium Salts.

The sodium salts of the above halogenated fatty acids were hydrolyzed in 0.1 N solutions using 15 cc. portions sealed in glass tubes as previously described.[1] In all cases, with the exception of sodium α-bromoisobutyrate, which was found to be very unstable, the temperature of hydrolysis was 70°. The values of K are based upon the silver nitrate necessary to precipitate the halide liberated at various time intervals by the usual titration formula for a monomolecular reaction.

$$K = 2.3/t_n\ [\log_{10}(T\infty - T_0) - \log_{10}(T\infty - T_n)].$$

Senter[2] has previously discussed the hydrolysis of sodium α-bromopropionate at 52.4° but has given no temperature coefficient. This work has been repeated to compare its stability with the stability of other salts at the same temperature. These experiments confirm his statement that the methyl group substituted in the α-position renders the compound less stable than the homologous sodium bromoacetate.

Sodium α-chloropropionate is found to be more stable than sodium α-bromopropionate, but it is less stable than sodium chloroacetate which was discussed in the previous paper.[3]

The hydrolysis of sodium β-chloropropionate, sodium β-bromopropionate, and sodium β-iodopropionate, which have not been studied before, produce hydracrylic acid under the conditions of these experiments. It was found that these salts are much more unstable than the isomeric α-halogen substituted compounds. Of the three, β-chloropropionic acid is the most stable, while little difference exists between the stability of β-bromopropionic acid and β-iodopropionic acid. This shows that the position of the halogen has a greater effect on the stability of the acid than does the identity of the halogen. In the latter two salts it will be noted

[1] Drushel and Simpson, *Loc. cit.*

[2] *Trans. Chem. Soc.*, **95**, 1827 (1909).

[3] This Journal, **39**, 2453 (1917).

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from Table I, D, E, that the reaction was about one-third complete before the solution reached the temperature of reaction. The great difference in the titrations with sodium hydroxide and silver nitrate is in accord with the recent work of Johannsen[1] on the formation of β-lactones.

TABLE I.—VELOCITIES OF HYDROLYSIS OF SODIUM α-CHLOROPROPIONATE, SODIUM α-BROMOPROPIONATE, SODIUM β-BROMOPROPIONATE, SODIUM β-IODOPROPIONATE, SODIUM β-CHLOROPROPIONATE AND SODIUM α,α-DIBROMOPROPIONATE IN 0.1 *N* SOLUTION AT 70°.

t (min.).	Cc. 0.1 *N* NaOH.	Cc. 0.1 *N* $AgNO_3$.	10^5K.	*t* (min.).	Cc. 0.1 *N* NaOH.	Cc. 0.1 *N* $AgNO_3$.	10^5K.
A. Sodium α-Chloropropionate.				B. Sodium α-Bromopropionate.			
0	0.10	0.10	...	0	1.22	1.30	..
180	2.45	2.98	126.0	15	3.60	3.77	1410
360	3.50	3.95	89.1	30	5.05	5.43	1270
780	6.48	6.90	85.5	60	7.60	7.85	1170
1620	9.93	10.43	82.5	90	9.10	9.20	1040
2250	11.23	11.70	78.5	120	9.65	10.03	945
3480	12.53	13.05	74.3	180	11.03	11.33	835
4800	13.12	13.42	62.5	240	11.50	11.65	682
∞	13.88	14.10	...	∞	13.98	14.15	...
C. Sodium β-Chloropropionate.				D. Sodium β-Bromopropionate.			
0	0.30	0.50	...	0	4.15	4.60	..
30	2.60	3.15	651	5	6.15	6.60	4670
60	3.95	4.90	581	10	7.20	7.85	4060
90	5.10	6.30	545	20	8.55	9.45	3490
120	5.90	7.30	505	30	9.77	10.33	2980
180	7.35	8.75	442	40	10.40	10.95	2690
300	9.00	10.40	353	65	11.40	11.95	2240
480	10.40	11.85	295	120	12.57	12.88	1620
∞	15.30	15.50	...	∞	14.10	14.30	..
E. Sodium β-Iodopropionate.				F. Sodium α,α-Dibromopropionate.			
0	4.13	4.55	..	0	0.80	0.80	...
5	6.12	6.55	4530	60	6.45	6.75	426
10	7.15	7.78	4040	150	11.35	12.00	368
20	8.87	9.42	3470	240	14.35	14.90	326
30	9.80	10.30	3010	420	17.85	18.45	264
40	10.35	10.97	2720	630	20.15	21.00	229
65	11.48	12.00	2240	1080	23.00	23.58	196
120	12.65	12.93	1650	1860	25.50	25.90	165
∞	14.10	14.30	..	∞	27.15	27.18	...

The hydrolysis of sodium α,α-dibromopropionate, in which both halogen atoms are removed, is of the same nature as sodium dichloroacetate that has been discussed in a previous paper.[2] It shows that the introduction of a second halogen into the α-position renders the compound much more stable.

In the hydrolysis of the sodium salts of α,β-dichloropropionic acid and

[1] *Ber.*, 48, 1262 (1915); *Chem. Zentr.*, II, 557 (1916).

[2] Drushel and Simpson, *Loc. cit.*

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α,β-dibromopropionic acid under the conditions of experiment only the β-halogen was replaced producing α-halogen substituted hydracrylic acid. In both cases it was found that the presence of the halogen in the α-position, which was not removed, greatly increased the stability of the salt.

The hydrolysis of sodium α-chlorobutyrate has not been studied previously. It was found to be more unstable than sodium chloroacetate and sodium α-chloropropionate. This is in accord with the work of Senter[1] on sodium α-bromobutyrate. This shows that the acid becomes more unstable with the increase in size of the group substituted into chloroacetic acid. The work of Senter on the hydrolysis of sodium α-bromobutyrate has been repeated to compare its stability with sodium α-chlorobutyrate and sodium α-bromoisobutyrate at 70°. Sodium α-chlorobutyrate was found to be more stable than the corresponding bromine compound, as is shown in Table II, C, D.

TABLE II.—SODIUM α,β-DICHLOROPROPIONATE, SODIUM α,β-DIBROMOPROPIONATE, SODIUM α-CHLOROBUTYRATE, AND SODIUM α-BROMOBUTYRATE IN 0.1 N SOLUTION AT 70°.

t (min.).	Cc. 0.1 N NaOH.	Cc. 0.1 N $AgNO_3$.	10^5K.	t (min.).	Cc. 0.1 N NaOH.	Cc. 0.1 N $AgNO_3$.	10^5K.
A. Sodium α,β-Dichloropropionate.				B. Sodium α,β-Dibromopropionate.			
0	0.10	0.15	..	0	0.75	1.10	...
720	2.20	2.65	25.0	60	2.10	2.65	190
1440	4.20	4.75	24.9	180	5.75	6.35	250
2880	7.50	7.90	24.6	360	8.60	9.10	226
4320	9.80	10.15	24.5	600	10.90	11.25	203
5760	11.18	11.60	24.0	840	11.70	12.15	176
7200	12.15	12.75	24.1	1380	13.20	13.66	157
9360	13.20	13.73	23.6	2100	14.60	15.03	160
∞	14.90	15.38	..	∞	15.10	15.50	...
C. Sodium α-Chlorobutyrate.				D. Sodium α-Bromobutyrate.			
0	0.20	0.20	...	0	1.35	1.55	..
120	2.10	2.40	134	15	4.70	5.20	2240
240	3.80	4.03	124	30	6.75	7.25	1970
420	5.65	5.90	116	60	9.25	9.88	1720
660	7.60	7.75	108	90	10.55	11.05	1510
1260	10.30	10.50	94	120	11.45	11.83	1380
1980	12.00	12.30	86	165	12.30	12.75	1280
2820	12.75	13.05	72	225	12.60	13.15	1080
∞	14.70	15.00	...	∞	14.10	14.28	..

The hydrolysis of sodium α-bromoisobutyrate was found to proceed very rapidly at room temperature. For this reason it was found necessary to carry out the hydrolysis in flasks at 25° and 35° in a water thermostat. At definite time intervals 15 cc. portions of the solution were drawn off in a pipet, added to ice water and immediately titrated in flasks which were chilled by an ice-salt bath. It will be noted from the tables that the

[1] *Trans. Chem. Soc.*, 95, 1827 (1909).

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values for K are fairly constant at 25° but at 35° decrease rapidly as the reaction proceeds. The values calculated for the hydrolysis at 70° are derived from the results at 35° by means of the temperature coefficient and can only approximate the true figures. It will also be evident that these temperature coefficients decrease rapidly as the reaction progresses.

TABLE III.—VELOCITIES OF HYDROLYSIS OF SODIUM β-CHLOROBUTYRATE IN 0.1 N SOLUTION AT 70°.

t (min.).	Cc. of 0.1 N NaOH.	Cc. of 0.1 N $AgNO_3$.	10^5K.
0	0.60	1.80	..
10	2.70	5.00	3020
20	4.50	7.17	2790
30	5.20	8.30	2490
45	7.15	10.23	2440
60	8.30	11.08	2440
75	9.00	11.90	2180
120	9.90	12.87	1760
∞	10.25	14.40	..

TABLE IV.—VELOCITIES OF HYDROLYSIS OF SODIUM α-BROMOISOBUTYRATE IN 0.1 N SOLUTION AT 25°.

t (min.).	Cc. of 0.1 N NaOH.	Cc. of 0.1 N $AgNO_3$.	10^5K.	Temp. coef. 25–35°.
0	0.95	1.45	...	..
15	1.90	2.50	685	4.75
30	3.00	3.40	662	4.53
60	4.30	5.00	667	4.27
120	6.60	7.30	646	4.03
180	7.95	8.85	633	3.78
270	9.30	9.90	628	3.52
360	10.05	10.50	663	3.12
∞	12.03	12.30	...	..

TABLE V.—VELOCITIES OF HYDROLYSIS OF SODIUM α-BROMOISOBUTYRATE IN 0.1 N SOLUTION AT 35° AND 70°.

t (min.).	Cc. of 0.1 N NaOH.	Cc. 0.1 N $AgNO_3$.	10^5K at 35°.	K at 70° (calc.).
0	2.20	2.80	..	..
5	3.50	4.30	3380	8.37
10	4.60	5.30	3100	5.87
20	6.30	7.05	2860	4.62
40	8.30	9.00	2750	3.60
60	9.37	10.07	2350	2.45
90	10.50	11.00	2140	1.76
120	11.05	11.57	2020	1.09
∞	12.10	12.43	..	..

Although β-chlorobutyric acid has not been previously studied, β-bromobutyric acid has been hydrolyzed at 38° by Johannsen. At this temperature he found that this acid decomposed to produce β-butyrolactone which he isolated and studied. The hydrolysis of sodium β-chlorobutyrate at 70° clearly indicates the formation of this lactone, by the great

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difference in titrations with sodium hydroxide and silver nitrate, but at this temperature this lactone has been partially hydrolyzed to form β-hydroxybutyric acid. The chlorobutyric acid is shown to be less stable than the isomeric α-chlorobutyric acid and the homologous β-chloropropionic acid.

This investigation in addition to showing the relative stability of several halogen substituted aliphatic acids, has furnished considerable evidence on the mechanism of the hydrolysis of their alkali salts.

The intermediate formation of a lactone in the hydrolysis of the β-halogen substituted aliphatic acids recently described by Johannsen[1] has been indicated in these results. We may also expect that an intermediate lactide has been formed similarly in the hydrolysis of α-substituted aliphatic acids under the conditions of these experiments.

New evidence has been found in support of the explanation advanced by Senter[2] to account for the decrease in the rate of reaction during the hydrolysis of sodium phenylchloroacetate. The best example of such a case found in this investigation is that of sodium α-bromoisobutyrate for which the following explanation is offered: In decinormal solutions the salts may be considered completely dissociated so that the hydrolysis takes place between water and the α-bromoisobutyric ion thus:

$$(CH_3)_2\,CBrCOONa \longrightarrow (CH_3)_2CBrCOO^- + Na^+$$

$$(CH_3)_2\,CBrCOO^- + HOH \longrightarrow (CH_3)_2COHCOO^- + H^+ + Br^-$$

As α-bromoisobutyric acid is not so highly dissociated as its sodium salt an equilibrium is formed between the α-bromoisobutyric and hydrogen ions and the undissociated acid:

$$(CH_3)_2CBrCOO^- + H^+ \rightleftharpoons (CH_3)_2CBrCOOH.$$

The undissociated α-bromoisobutyric acid may also be hydrolyzed but Senter[2] has shown that acids react in this manner much slower than the ions. De Barr[3] has shown that high temperatures are required to decompose the free acids, so we should expect that the latter reaction would be negligible at sufficiently low temperatures and then the value of K should be constant. Such a condition has been realized in the hydrolysis of sodium α-bromoisobutyrate at 25°, but at 35° the decreasing values of K indicate the activity of undissociated α-bromoisobutyric acid in the reaction. This experiment also shows that hydrobromic acid formed by the reaction does not act as a negative catalyst in this case, although Senter[4] has been able to measure its influence in the hydrolysis of α-bromopropionic acid, phenylchloroacetic acid, and phenylbromoacetic acid.

[1] *Loc. cit.*

[2] *Trans. Chem. Soc.*, **107**, 908 (1915).

[3] *Am. Chem. J.*, **22**, 336 (1899).

[4] *Trans. Chem. Soc.*, **99**, 1049 (1911); **107**, 908 (1915); **109**, 681 (1916).

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Some very interesting speculations are found in applying this theory to the hydrolysis of salts of dihalogen substituted aliphatic acid in which both halogens are replaced. Examples of such salts are sodium α,α-dibromopropionate of this article and sodium dichloroacetate previously discussed.[1] The equations for the hydrolysis of the latter salt according to the above theory would be written thus:

$$CHCl_2COONa \longrightarrow CHCl_2COO^- + Na^+$$
$$CHCl_2COO^- + HOH \longrightarrow CHOCOO^- + 2H^+ + 2Cl^-$$
$$CHOCOO^- + H^+ \rightleftharpoons CHOCOOH$$
$$CHCl_2COO^- + H^+ \rightleftharpoons CHCl_2COOH$$
$$CHCl_2COOH + HOH \longrightarrow CHOCOO^- + 2H^+ + 2Cl^-$$

From this it is evident that the concentration of undissociated dichloroacetic acid is relatively great compared with the concentration of chloroacetic acid during the hydrolysis of sodium chloroacetate due to the greater number of hydrogen ions. This explains the unusually large decrease in the rate of reaction as hydrolysis proceeds.

If this hypothesis is correct it explains the stability of α,β-dichloropropionic acid, chloroacetic acid, and iodoacetic acid previously described, toward water at 70°, as their rates of reaction are constant at this temperature. From these experiments it is evident that there is no secondary action due to the hydrolysis of undissociated halogen substituted acid at 70°. This point must be proved by later investigation.

Summary.

From the results of this work the relative stability of the several halogen substituted and propionic and butyric acids is expressed by the following table:

TABLE VI.—RELATIVE STABILITIES.

Propionic Acid Series.	
β-Bromopropionic acid	1.0
β-Iodopropionic acid	1.03
α-Bromopropionic acid	3.31
β-Chloropropionic acid	7.17
α,α-Dibromopropionic acid	10.96
α,β-Dibromopropionic acid	18.68
α-Chloropropionic acid	37.06
α,β-Dichloropropionic acid	186.8
Butyric Acid Series.	
α-Bromoisobutyric acid	1.0
β-Chlorobutyric acid	277.0
α-Bromobutyric acid	374.0
α-Chlorobutyric acid	6171.0

1. Chlorine substituted aliphatic acids are more stable than the analogous bromine or iodine compounds.

[1] Drushel and Simpson, *Loc. cit.*

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2. The evidence indicates that some iodine substituted aliphatic acids are more stable than the analogous bromine compounds.

3. α-Halogen substituted acids are more stable than isomeric β-halogen substituted acids.

4. The effect of position on the stability of a halogen substituted acid is greater than the identity of the halogen.

5. The replacement of a hydrogen atom on the carbon atom carrying the halogen by an aliphatic radicle renders the acids less stable.

6. The replacement of a second hydrogen atom on the carbon atom carrying the halogen by an aliphatic radicle greatly decreases the stability of the acid.

7. The larger the aliphatic group substituted the more unstable the acid becomes.

8. The presence of a second halogen in the α-position of the acid (irrespective of the replacement of that second halogen) renders the removal of the first halogen in either the α- or β-positions more difficult.

The writer is indebted to W. A. Drushel for his coöperation in this work.

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON UNIVERSITY.]

THE NEUTRAL AMMONIUM SALTS OF ORGANIC ACIDS AND THEIR SUBSTITUTED DERIVATIVES.

[SEVENTH COMMUNICATION.[1]]

BY LEROY MCMASTER AND LETA WRIGHT.

Received January 22, 1918.

This work is a continuation of the preparation and investigation of the properties of neutral ammonium salts of organic acids and their substituted derivatives. The salts described in this paper were prepared by the same general method as was used in the previous investigations, *i. e.*, by passing dry ammonia into solutions of the acids in anhydrous organic solvents. We have thus prepared and studied the ammonium salts of 1,2,3-methylhydroxybenzoic, 1,3,4-methylhydroxybenzoic, 1,4,3-methylhydroxybenzoic, 1,2,4-dihydroxybenzoic, 1,2,5-dihydroxybenzoic, 1,2,4-dinitrobenzoic, *o*-nitrocinnamic, *m*-nitrocinnamic, *p*-nitrocinnamic, α-naphthoic, β-naphthoic, *m*-nitrobenzenesulfonic, *m*-aminobenzenesulfonic (metanilic) 1,2,4-nitrotoluenesulfonic, 1,4-naphthylaminesulfonic (naphthionic), 1,4-naphtholsulfonic, 1,5-naphtholsulfonic, benzilic, oxanilic and phenyl-

[1] For previous papers on this subject see *Am. Chem. J.*, **49**, 84–7 (1913); *Chem. News*, **108**, 136–7 (1913); *Am. Chem. J.*, **49**, 294–301 (1913); *Chem. News*, **108**, 182–3, 193–4 (1913); THIS JOURNAL, **36**, 742–7 (1914); *Chem. News*, **110**, 212–4 (1914); THIS JOURNAL, **36**, 1916–25 (1914); *Chem. News*, **110**, 224–8 (1914); THIS JOURNAL, **37**, 2181–8 (1915); *Chem. News*, **112**, 187–9 (1915); THIS JOURNAL, **38**, 1785–1803 (1916); *Chem. News*, **114**, 217–221, 224–227, 238–239 (1916).

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propiolic acids. After the salts were precipitated and tested for neutrality they were quickly filtered by suction, washed with anhydrous ether and allowed to stand for a short time in a vacuum desiccator.

Substituted Benzoic Acids.

Methylhydroxybenzoic Acids.

There are 10 acids of the formula $CH_3C_6H_3(OH)CO_2H$ known,[1] and are sometimes called the cresotinic acids. We have been able to procure from Kahlbaum the 1-methyl-2-hydroxy-3-carboxylic acid, the 1-methyl-3-hydroxy-4-carboxylic acid, and the 1-methyl-4-hydroxy-3-carboxylic acid. All three of them gave neutral ammonium salts.

Ammonium Salt of the 1-Methyl-2-hydroxy Acid.—Hübner[2] worked with some of the salts of this acid, but not with the ammonium salt. No record can be found of its preparation. A very stable salt is formed when an ether solution of the acid is saturated with dry ammonia. It dries in the form of pink-tinted needles which tend to adhere to each other to form cotton-like masses. The salt is exceedingly soluble in ethyl alcohol and will not precipitate from a mixture made of equal parts of alcohol and ether. It is also soluble in methyl alcohol and acetone, slightly soluble in ethyl acetate, and insoluble in ether, chloroform and benzene. The aqueous solution of the salt does not hydrolyze. The salt is not hygroscopic and does not lose ammonia when dried at 100°. Moist air causes it to lose ammonia slowly.

Calc. for $CH_3.C_6H_3(OH)CO_2(NH_4)$: N, 8.29%. Found: 8.31%.

Ammonium Salt of the 1-Methyl-3-hydroxy Acid.—No reference to this salt is made in the literature. A quantitative yield was obtained when it was precipitated from an ether solution of the acid. It formed in beautiful, pure white needles which, like those of the preceding salt, formed into lustrous, cotton-like masses. When the ammonia was passed into the acid solution, an amorphous, semi-transparent mass formed at first, which very soon changed to a voluminous precipitate of needles, which are not deliquescent. The salt is soluble in methyl and ethyl alcohols and acetone, slightly soluble in ethyl acetate, and insoluble in ether and benzene. It is not quite as stable as the preceding salt, since moist air decomposes it rather readily. Dry air at 50° for 1 hour has no effect on the salt, while at 100° it decomposes slightly within 30 minutes. Its aqueous solution remains neutral and the salt does not hydrolyze.

Calc. for $CH_3.C_6H_3(OH)CO_2(NH_4)$: N, 8.29%. Found: 8.27%.

Ammonium Salt of the 1-Methyl-4-hydroxy Acid.—When ammonia was passed into an ether solution of the acid, there was first formed an amorphous mass, which soon changed to a white, cotton-like mass of needles.

[1] *Ber.*, **16**, 1966 (1883).

[2] *Monatsh.*, **15**, 725 (1894).

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This was similar to the action taking place in the preparation of the two preceding salts. We attempted to prepare this salt also in an ethyl acetate solution of the acid since we had found that the 1,2,3- and the 1,3,4-salts were only slightly soluble in that solvent. No yield was obtained as the salt was found to be readily soluble in ethyl acetate. It is also very soluble in water, methyl and ethyl alcohols and acetic acid but only slightly soluble in benzene. It is not hygroscopic and its neutral aqueous solution does not hydrolyze.

The salt is a little less stable than its two preceding isomers, but even as that it is quite stable. At ordinary temperatures it does not decompose in dry air, and when heated at 50° for 1 hour it decomposes but slightly. Moist air at ordinary temperatures decomposes it slowly. When heated to 100°, the salt decomposes into ammonia and the acid. The literature makes no mention of this salt so far as we can find.

Calc. for $CH_3.C_6H_3(OH)CO_2(NH_4)$: N, 8.29%. Found: 8.30%.

All three of these salts have a faint phenol odor, which is also characteristic of the free acids. It should be noted that all of them precipitate from ether solutions of the acids in the form of needle-like crystals. It has been found that a majority of the ammonium salts prepared in ether form as non-crystalline bodies.

Dihydroxybenzoic Acids.

Ammonium 1,2,4-Dihydroxybenzoate.—Since the acid is called resorcylic acid, another name for the salt would be ammonium resorcylate. The acid formed an orange-red solution with ether, from which the salt precipitated as a delicately colored pink powder. It precipitated immediately and in rather voluminous quantities. This delicately colored salt shared with the free acid the property of making highly colored solutions. With water a light brown solution was formed, which, upon the addition of sodium hydroxide solution, changed to a dark rich, red-brown color. Ammonium resorcylate is soluble in both methyl and ethyl alcohols, but is insoluble in ethyl acetate, ether, benzene and acetone. It decomposes slightly in dry air at 50° after 40 minutes, and rapidly gives off ammonia when the temperature has been 100° for a half hour. Its solution with water remains neutral for some time. The salt is not hygroscopic.

Calc. for $C_6H_3(OH)_2CO_2(NH_4)$: N, 8.19%. Found: 8.25%.

Ammonium 1,2,5-Dihydroxybenzoate or Ammonium Gentisate.—The acid formed with ethyl acetate a dark brown solution, from which ammonia precipitated a dark, gelatinous, pasty mass; but, on shaking and on further addition of ammonia, this gelatinous mass was replaced by a light brown, amorphous powder. The color became lighter, and when precipitation was complete the precipitate was almost white. When it was dried and powdered it was a very slightly colored substance, but, after standing for

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5 months, the color was somewhat darker, probably on account of slight decomposition. The salt forms a neutral solution with water, and is soluble in acetic acid and methyl alcohol, slightly soluble in ethyl alcohol, but insoluble in ether, ethyl acetate, benzene and chloroform. Acetone very slightly dissolves it. It does not lose ammonia on exposure to dry air at 50°, and even at 100° there is but very little loss after some length of time. The salt is not deliquescent.

Calc. for $C_6H_3(OH)_2CO_2(NH_4)$: N, 8.19%. Found: 8.19%.

A Dinitrobenzoic Acid.

Ammonium 1,2,4-Dinitrobenzoate.—The ammonium 1,3,5-dinitrobenzoate[1] has been prepared in this laboratory in ether solution and found to be a white, amorphous powder, having a slight yellowish tinge. We have also prepared the 1,2,4-salt in ether. When the ammonia was passed into an ether solution of the acid, a transparent, yellowish, gelatinous mass was first formed. This soon changed to a yellowish white, flocculent precipitate and then to an amorphous powder. After drying, the salt was found to have the same color as the 1,3,5-body. It is not as stable in the air as the latter salt for it gives off ammonia very slowly in dry air and rapidly in moist air. The temperature of the dry air does not seem to affect the rate of decomposition of the salt. The 1,3,5-salt is stable in dry air and loses its ammonia only very slowly in moist air. Neither salt is deliquescent. The aqueous solution of the 1,3,5-salt does not hydrolyze even on standing for several days, while that of the 1,2,4-salt is neutral at first but becomes acid after several hours. A peculiar difference between the two salts is to be observed in their solubilities. The 1,3,5-salt is soluble in all the ordinary organic solvents except ether, though not very readily in acetone; the 1,2,4-salt is practically insoluble in all the organic solvents except methyl alcohol.

In determining the ammonium nitrogen high results were always obtained so we made determinations of the total nitrogen.

Calc. for $C_6H_3(NO_2)_2CO_2(NH_4)$: total N, 18.35%. Found: 18.32%.

The Nitrocinnamic Acids.

Ammonium *o*-Nitrocinnamate.—The free acid was found to be insoluble in all the usual organic solvents except acetone, in which it is very slightly soluble. Moreover, the ammonium salt is very soluble in most of the solvents, except ethyl acetate and benzene in which it is insoluble. Acetone dissolves the salt but slightly.

When ammonia was passed into a suspension of the acid in ethyl alcohol, a precipitate formed which went into solution at once. It could not be reprecipitated by any reagent obtainable since its solubility in ethyl alcohol is so great. When a suspension of the acid in ether was saturated

[1] THIS JOURNAL, 38, 2187 (1915).

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with ammonia, a yellow, amorphous precipitate, lighter in color than the free acid, which has a rich yellow color, was formed. Tests for neutrality and analysis proved this precipitate to be the neutral ammonium salt. The salt is not deliquescent and its aqueous solution does not hydrolyze. In dry air the salt does not lose ammonia but does so in moist air.

Calc. for $C_8H_6(NO_2)CO_2(NH_4)$: ammonium N, 6.67%. Found: 6.62%.
Calc. for $C_9H_{10}N_2O_4$: total N, 13.33%. Found: 13.31%.

Ammonium *m*-Nitrocinnamate.—The free acid is insoluble in the organic solvents, except in ethyl acetate. When an ethyl acetate solution of the acid was saturated with ammonia, a white, curdy mass formed, which changed almost at once to a very fine, noncrystalline substance. It was very difficult to dry this precipitate. It was not possible to drain off the solvent, even with strong suction; so the pasty mass was placed for about an hour in a vacuum desiccator. It was then ground to a fine, chalky powder, which loses its ammonia very slowly in a moist atmosphere. The salt is not hygroscopic, and its aqueous solution remains neutral for several hours. The salt was found to be a rather difficultly soluble compound. It is most soluble in acetic acid, and only sparingly so in water, methyl alcohol and acetone. It is insoluble in ethyl alcohol, ether and benzene.

The salt decomposes very slowly in hot, dry air. At 50° for 30 minutes the decomposition is slow, but at 100° for 15 minutes ammonia is rapidly given off. Analysis of the salt prepared in ethyl acetate proved it to be the neutral body.

Calc. for $C_8H_6(NO_2)CO_2(NH_4)$: total N, 13.33%. Found: 13.34%.

Ammonium *p*-Nitrocinnamate.—As in the two preceding cases, difficulty was encountered in getting the acid into solution. The acid was so very slightly soluble in all the organic solvents that we tried a suspension of it in ethyl alcohol; but, as was the case with the *o*-salt, this ammonium salt was so soluble in the alcohol that it would not precipitate nor could we precipitate it by adding large amounts of other solvents to the alcohol solution. When a suspension of the acid in ether was tried, we obtained a fine, yellow powder of the neutral ammonium salt. This salt was soluble in water with difficulty, readily soluble in methyl alcohol, ethyl acetate and ethyl alcohol, slightly soluble in acetone but insoluble in ether, chloroform and benzene. It decomposed at 50°. The salt is not hygroscopic and its aqueous solution hydrolyzes very slowly.

Calc. for $C_8H_6(NO_2)CO_2(NH_4)$: total N, 13.33%. Found: 13.32%.

Most of the neutral ammonium salts so far prepared have been found to be readily soluble in water, but these three nitro-salts were unusually difficult to dissolve in water. Ammonium cinnamate,[1] previously prepared, was

[1] *Am. Chem. J.*, 49, 300 (1913).

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found to be much more soluble in water than these three nitro-derivatives. However, the ammonium nitrocinnamates resemble the ammonium cinnamate in many respects. When ammonia is conducted into an ether solution of cinnamic acid, a gelatinous precipitate is first obtained which later changes to an amorphous form. The same phenomenon occurs in the formation of the *m*-nitrocinnamate in ethyl acetate but not in the formation of the *o*- and *p*-salts in ether. We could find no record of any of these salts having been previously prepared even in aqueous solution.

The Naphthoic Acids.

Ammonium α-Naphthoate.—The barium, calcium and silver salts of α-naphthoic acid have been prepared by Hofman,[1] but no reference to the ammonium salt can be found. The acid is not soluble in ether, but is easily soluble in hot ethyl alcohol. However, the ammonium salt is so very soluble in alcohol that it is impossible to precipitate it in this medium even in the presence of a large amount of ether. It was, therefore, necessary to pass the ammonia into a suspension of the acid in ether, whereupon the ammonium salt quickly formed as a fine, white powder. The aqueous solution is neutral and does not hydrolyze for a number of hours. The salt is not hygroscopic and does not give off ammonia in dry air at room temperature. Moist air decomposes the salt slowly. When heated to 50° in dry air decomposition is perceptible after 40 minutes. After 10 minutes at 100° it is rapidly broken up, giving off ammonia freely.

The salt is very soluble in methyl and ethyl alcohols, moderately soluble in acetone and acetic acid, and insoluble in ether, chloroform, ethyl acetate and benzene.

Calc. for $C_{10}H_7CO_2(NH_4)$: N, 7.41%. Found: 7.40%.

Ammonium β-Naphthoate.—A number[2] of the salts of β-naphthoic acid have been made and studied, but there is no record of the neutral ammonium salt. The acid is readily soluble in both ether and ethyl alcohol and the ammonium salt can be prepared in either solvent. When prepared in ether it forms as a pure white, amorphous powder. Its aqueous solution does not hydrolyze. The salt dries quickly, is not hygroscopic, and does not give off ammonia in dry air at ordinary temperatures. In moist air ammonia is given off. At 50° in dry air for 30 minutes the salt decomposes, and at 100° marked decomposition takes place within 15 minutes.

The salt is insoluble in ethyl acetate, chloroform, acetone, ether and benzene and only slightly soluble in ethyl alcohol. Except for certain differences in solubility, the properties of this salt closely resemble those of the α-salt.

Calc. for $C_{10}H_7CO_2(NH_4)$: N, 7.41%. Found: 7.39%.

[1] *Ber.*, 1, 39 (1868).

[2] Vieth, *Ann.*, 180, 305 (1876); Merz and Mühlhäuser, *Z. Chem.*, 5, 70 (1869).

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Sulfonic Acids.

The literature mentions a few ammonium salts of the sulfonic acids prepared in aqueous solution, but their properties are very inadequately described. Having never applied our general method to the preparation of ammonium salts of this class of acids, we turned our attention to the preparation of some of them. Our results show that they can thus be readily made.

Ammonium *m*-Nitrobenzenesulfonate.—Limpricht[1] describes this salt as crystallizing in clear leaflets without water of crystallization, but gives nothing further of its properties. We prepared this salt in an ether solution as a white, bulky, noncrystalline compound. The salt dries quickly in the air and is very stable. It is not deliquescent, and does not give off ammonia in moist air nor in dry air at any temperature up to 100°. At this temperature there is no evidence of any decomposition. The salt is soluble in water, to which it imparts a neutral reaction for at least several days. We could not prepare it in an ethyl alcohol solution on account of its solubility in that solvent. The salt is slightly soluble in methyl alcohol, and insoluble in chloroform, ether and acetone.

Calc. for $C_6H_4(NO_2)SO_3(NH_4)$: ammonium N, 6.36%. Found: 6.37%.

Ammonium *m*-Aminobenzenesulfonate or Ammonium Metanilate.—It was found that the acid is insoluble in ether and soluble in alcoholic ammonia. The ammonium salt was probably formed, but would not precipitate on account of its solubility in the ethyl alcohol. After saturating this alcohol solution with ammonia, an attempt was made to precipitate the salt by adding an excess of ether. A white, colloidal product resulted, which could not be filtered even on an alundum crucible. The mixture was allowed to stand for a number of days and, after the ether had evaporated, a clear, yellowish solution remained. Upon further evaporation, the alcoholic solution became darker in color and finally turned red. No crystals separated until practically all the solvent had evaporated, whereupon large, dark red, thick plates appeared. They gave a neutral reaction when dissolved in water. This aqueous solution, which was reddish in color, did not hydrolyze until it had stood for 2 days. The salt was stable at ordinary temperatures and slowly decomposed in dry air at 50°. It was decomposed readily in moist air.

Calc. for $C_6H_4(NH_2)SO_3(NH_4)$: ammonium N, 7.37%. Found: 7.38%.

Ammonium 1,2,4-Nitrotoluenesulfonate.—Jenssen[2] mentions this salt but tells nothing about it except that it crystallizes in long, fine needles, and is not decomposed at 190°. An attempt was made to precipitate it in ethyl alcohol, because it was thought that a better crystalline form could be obtained from alcohol than from ether. But though there was some

[1] *Ann.*, **177**, 73 (1875).
[2] *Ibid.*, **172**, 232 (1874).

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precipitation, it took place very slowly and very incompletely. The free acid was found to be insoluble in ether, but the ammonium salt came out beautifully when a suspension of the acid in ether was saturated with ammonia. The white precipitate was amorphous in form, and all of the free acid was converted into the salt. There was a slight amount of heat generated in this precipitation. This is unusual for it has been found that almost always there is no heat generated when ether is used. The salt is not deliquescent. In dry air at 50°, there was evidence of some decomposition of the salt after 30 minutes, but the rate was not much increased when the temperature was raised to 100°. Moist air decomposed it slowly. It was found to be slightly soluble in methyl alcohol, still less so in acetone and insoluble in ether and chloroform. It is slightly soluble in ethyl alcohol. The aqueous solution is neutral and does not hydrolyze readily.

Calc. for $CH_3.C_6H_3(NO_2)SO_3(NH_4)$: ammonium N, 5.98%. Found: 6.02%.

The ammonium nitrotoluenesulfonate is less stable than the nitrobenzenesulfonate, but in other ways the salts resemble each other. The ammonium nitrotoluenesulfonate has a peculiar odor which is not noticeable with the ammonium nitrobenzenesulfonate.

Ammonium 1,4-Naphthylaminesulfonate.—The ammonium salt of this acid known as naphthionic acid is not mentioned in the literature. It was found that the acid is a very insoluble substance. A suspension of the acid in ethyl acetate was used for making the ammonium salt. It was easy to see it changing over to the salt, for the acid is a chalky white, amorphous powder, while the ammonium salt is pinkish brown in color and possesses a distinct crystalline form. Ammonium naphthionate is soluble in methyl and ethyl alcohols, and warm water. It is only slightly soluble in cold water. In solution it gives a red and blue fluorescence, which is characteristic of the salts[1] of naphthionic acid. The lead salt crystallizes in small, red grains, while the crystals of the ammonium salt are small pinkish brown grains. The ammonium salt forms a neutral aqueous solution which does not hydrolyze within 3 hours. The salt is stable in dry air at 50°, but after 30 minutes at 100°, there is a faintly perceptible change imparted to the color of sensitive red litmus paper. Moist air causes the salt to give off ammonia. It does not deliquesce.

Calc. for $C_{10}H_6(NH_2)SO_3(NH_4)$: ammonium N, 5.83%. Found: 5.86%.

Ammonium 1,4-Naphtholsulfonate.—There is no reference to this salt in the literature, though a number of other salts of the free acid, which is called "Neville, Winther's acid," have been investigated.[2] The acid is a very insoluble substance, but methyl alcohol and ethyl alcohol dissolve it slightly. The salt is very soluble in methyl alcohol, but was precipitated by adding to the solution 10 times its volume of anhydrous ether. It was

[1] Piria, *Ann.*, **78**, 31 (1851).

[2] *Ber.*, **13**, 1949 (1880); *Ann.*, **273**, 107 (1893).

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almost impossible to free the salt of the excess of solvent. It rapidly decomposed in dry and in moist air at ordinary temperatures, and its water solution, though neutral for about 3 minutes, quickly hydrolyzed and gave an acid reaction. The salt is a light brown powder, a "cocoa" colored substance, while the free acid is slightly pink. By the time the salt was thoroughly dry (a period of several days), analysis showed that it had greatly decomposed.

The salt was also prepared in a benzene suspension of the acid, and the same brown colored powder was obtained. It dried very much more readily than the methyl alcohol product, but it gave off ammonia very rapidly. It was analyzed a few hours after it was made, and the results showed that it had then more than half decomposed, although it had been either in a vacuum desiccator or in a tightly stoppered bottle during the meantime. At first a water solution of the freshly prepared salt showed a neutral reaction, but it soon hydrolyzed. The salt is insoluble in ether, chloroform, acetone, ethyl acetate and benzene.

Ammonium 1,5-Naphtholsulfonate.—It was thought best to prepare this salt from an ether suspension, since it was found that it was, like the 1,4-salt, very soluble in methyl alcohol, which is the only medium in which the free acid is easily soluble. The salt was quickly filtered and dried. It dried quickly to a finely divided, brownish powder, an aqueous solution of which gave a neutral test for a period of 10 minutes. Dry air at ordinary temperatures does not decompose it within a period of 15 minutes, but after that it does. It quickly decomposes at 50° in dry air, and moist air at ordinary temperatures decomposes it readily.

Both this 1,5-salt and the salt of Nevile, Winther's acid are very soluble in methyl alcohol, somewhat soluble in ethyl alcohol, and insoluble in ether, ethyl acetate, benzene, chloroform and acetone. The 1,4-salt is also insoluble in acetic acid, while the 1,5-salt shows a slight solubility in this medium. The latter salt, as well as the former, lost ammonia so readily that one analysis showed only 2.25% N. The correct value is 5.81%.

Other Acids.

Ammonium Benzilate.—There is no record of this salt ever having been prepared, though other salts of benzilic acid have been studied.[1] The free acid is soluble in methyl and ethyl alcohols, ether and ethyl acetate, but ammonia will not precipitate the salt from any of these solutions. In ether, a precipitate did form at first as an amorphous, white powder, but on addition of more ammonia this changed to a sticky half-transparent mass, which in turn dissolved when still more ammonia was added. Finally a benzene suspension was treated with ammonia. The fine, white needles of the free acid were very rapidly changed over into a yellowish mass exactly like that encountered in one stage of the ether solution treatment.

[1] Symons and Zincke, *Ann.*, 171, 131 (1874).

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This mass did not change in appearance materially for a period of 3 hours, during which time ammonia was constantly bubbled through the solution. At the end of that time the flask was removed and stoppered. It was allowed to stand for 2 days and then small transparent crystals were seen distributed over the bottom and sides of the flask. The mass that had been soft and sticky had become hard, and when broken up it was found to consist of the same small granular crystals which coated the flask. These crystals were filtered and dried in a vacuum for a short time, and tested for neutrality and stability. Their aqueous solution was neutral. They are not deliquescent. Moist air slowly decomposes the salt, and dry air at 50° causes it to lose ammonia after 30 minutes.

Calc. for $(C_6H_5)_2C(OH)CO_2(NH_4)$: N, 5.71%. Found: 5.71%.

This diphenylhydroxyammonium acetate resembles very much more closely the salts of phenylacetic acid and its substituted derivatives than it does that of glycolic acid itself. It has been found by one of us that ammonium phenylacetate and the substituted phenylacetates are stable salts, some of which are yellowish in color; they give off ammonia slowly in moist air, and they can all be prepared in alcohol. This is not true of the benzilate and that fact constitutes the only point of resemblance between the benzilate and glycolate itself. Ammonium glycolate[1] rapidly loses ammonia in the air and is hygroscopic. Also, a water solution of ammonium glycolate hydrolyzes very readily, and one of ammonium benzilate does not.

Ammonium Oxanilate.—This salt has been prepared and some of its properties studied.[2] It is described as plates, slightly soluble in cold water and cold alcohol, but very soluble in hot water and hot alcohol. It is also stated that it begins to lose its ammonia at 190°.

The neutral salt can be precipitated from an ether suspension of the acid in the form of a curdy mass or as a flaky precipitate from a methyl or ethyl alcohol solution of the acid. Considerable heat was developed when the ammonia was passed into the alcohol solutions and it was necessary to keep the solutions cold. Flaky, yellowish white crystals precipitated. When perfectly dry, the salt is composed of fine, white needles.

The salt is soluble with difficulty in cold water, to which it imparts a neutral reaction. The aqueous solution does not hydrolyze. It is only slightly soluble in methyl and ethyl alcohols, and insoluble in acetone, ether and benzene. The salt is not deliquescent and gives off no ammonia in dry air until heated above 100°. Laurent and Gerhardt found that at 190° this salt began to lose ammonia and at the same time a little aniline was formed and finally there remained oxanilide. On gently heating, we also found aniline to be formed. In moist air ammonia is slowly given off.

[1] McMaster and Magill, THIS JOURNAL, 38, 1788 (1916).

[2] Laurent and Gerhardt, *Ann.*, 68, 20 (1848); Aschan, *Ber.*, 23, 1821 (1890).

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Calc. for $NH(C_6H_5)CO.CO_2(NH_4)$: total N, 15.38%. Found: 15.36%.

Ammonium Phenylpropiolate.—Phenylpropiolic acid, which contains a triple bond, is the first acid of its type whose ammonium salt has been studied in this laboratory. There is no record of the salt having been made elsewhere. It was precipitated in an ether solution of the free acid. A little heat was developed during the saturation with ammonia, which is an unusual occurrence with ether solutions. The salt is a pure white powder, having a slight odor. It is somewhat soluble in ethyl alcohol, very soluble in methyl alcohol, and insoluble in chloroform, acetone, benzene and ether. An aqueous solution is neutral for about 2 hours, after which time it slowly hydrolyzes and gives an acid reaction. Moist air causes it to lose ammonia, but in dry air at 50° it remains unchanged for about 1 hour before it begins to lose ammonia slowly. The salt is not hygroscopic.

Calc. for $C_6H_5C:CCO_2(NH_4)$: N, 8.59%. Found: 8.62%.

Work is still in progress in this laboratory on the ammonium salts of organic acids.

St. Louis, Mo.

[Contribution from the Division of Agricultural Biochemistry, University of Minnesota.]

AN OPTICAL METHOD FOR THE DETERMINATION OF MALIC AND TARTARIC ACIDS IN THE SAME SOLUTIONS.[1]

By J. J. Willaman.

Received January 25, 1918.

Introduction.

For several years the question of optical methods for malic and for tartaric acids has been before the conventions of the Association of Official Agricultural Chemists. Such progress was made in the case of malic acid that a polariscopic method was incorporated in the official methods of the Association in 1916.[2] The method involves the increase in optical activity caused by uranyl acetate, a reaction first observed by Walden.[3] A method for tartaric acid was not so successfully evolved, although its optical activity is likewise strongly increased by uranyl acetate.[4]

Where both acids occur in the same solution, a special problem arises. There is no way now known by which they can be separated quantitatively; hence any method for their determination must depend upon

[1] Published with the approval of the Director as Paper No. 111, Journal Series Minnesota Agricultural Experiment Station.

[2] "Methods of Analysis," *J. Assoc. Off. Agr. Chemists*, 1916.

[3] Walden, "Über ein neues, die Drehungsgrösse steigerndes Mittel.," *Ber.*, [3] 30, 2889–2895 (1897).

[4] P. B. Dunbar, "The Determination of Tartaric Acid," *U. S. Dept. Agr. Bur. Chem. Circ.*, 106 (1912).

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two factors applied to the same solution. In 1911, Yoder[1] suggested, but did not work out in detail, that when these two acids are present in the same solution, the titre and the optical activity as increased by uranyl acetate would give data for calculating the amount of each acid. The difficulty here, of course, is in having only these two acids present and in the free state. In 1912, Dunbar[2] published a method for these two acids, employing the activated rotatory power together with either the amount of oxalic acid formed by the permanganate oxidation of these acids, or the amount of permanganate reduced. The method has been unsuccessful in the hands of other workers, due, no doubt, to the fact that in natural products there are always other substances present which reduce permanganate and form oxalic acid. At the 1913 meeting of the Association of Official Agricultural Chemists, Gore[3] reported an attempt to use two optical activators, uranyl acetate and ammonium heptamolybdate. The former increases the negative rotation of *l*-malic acid and the positive rotation of *d*-tartaric acid; the latter reverses the direction of rotation of *l*-malic, giving a strong positive rotation for both acids. Gore found, however, that linear relations do not exist between the amount of acid present and the optical activity, especially in the case of the tartaric acid. Hence the proposed method was untenable. He concluded his discussion with the statement, "No method for the estimation of the two acids in the presence of each other by polarimetric means alone is in sight at present."

It occurred to the writer, however, that whether strictly linear relations existed or not, a given set of conditions could be chosen and adhered to in constructing tables or curves with known amounts of pure malic and tartaric acids, which curves could then be used for the determination of unknown quantities of these acids. The method herein described has such an origin. Nothing new is claimed for any of the processes; but the combination of processes chosen has resulted in a new, simple, and satisfactory optical method for the determination of malic and tartaric acids in natural products.

Experimental Study of Factors Involved.

The development of the method involved two phases: first, the ascertaining of whether a given set of necessary conditions will always give the same results, and second, the search for that combination of conditions and processes that will give results satisfactory from the standpoints of accuracy, ease of manipulation, and applicability to materials from

[1] P. A. Yoder, "A Polarimetric Method for the Determination of Malic Acid and its Application in Cane and Maple Products," *J. Ind. Eng. Chem.*, 3, 563–574 (1911).

[2] P. B. Dunbar, "The Determination of Malic and Tartaric Acids in the same Solution," *U. S. Dept. Agr. Bur. Chem. Circ.*, 105.

[3] Gore, *J. Assoc. Off. Agric. Chemists*, 1, 120–130 (1915).

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varied sources. The first point was answered affirmatively by a review of the published experiences of the various workers in this field, and by some preliminary trials by the writer. The second point necessitated a careful study of all the factors which affect the optical activities of the acids under the proposed treatment. The simplest way to explain the choice of details finally decided upon is to enumerate and discuss each factor separately.

1. **Kind of Activator.**—A number of compounds of uranium, tungsten, molybdenum, boron, titanium, etc., have been found which increase the optical activity of certain organic compounds. Uranyl acetate, $UO_2(C_2H_3O_2)_2.2H_2O$, and ammonium heptamolybdate, $(NH_4)_6Mo_7O_{24}.4H_2O$, were chosen for the present work, because (1) they give very marked increases in the rotatory power of malic and tartaric acids, (2) they have been worked with enough to show their applicability to the method in hand, and (3) they can be obtained as pure salts fairly readily. Yoder[1] found uranyl nitrate to be inferior to the acetate because of the mineral acid produced by hydrolysis.

2. **Kind of Acids Affected.**—Walden[1] showed that it is the optically active, dicarboxylic oxy-acids that are affected by these metals; other oxy-acids, however, are not excluded. Thus malic and tartaric are markedly affected; citric[2] is to a certain degree, and any considerable quantity of it will interfere with the present method; lactic[3] is affected very slightly, but not enough to interfere; a few aromatic acids are affected, but are not commonly found in natural products. Hence citric acid is the only one to be guarded against in applying the present method.

3. **Effect of Substances Other than Acids.**—Yoder[1] found that sugars in concentrations up to five times that of the malic acid do not interfere; Dunbar and Bacon[4] found that normal solutions of sucrose and invert sugar give slightly lower readings in the presence of uranyl acetate. In the present method the sugars are excluded by removing the acids as the barium salts. Ammonium sulfate increases the readings with molybdenum and decreases those with uranium. Although ammonium sulfate is not present in appreciable amounts in natural products, it is present in the following method, due to excess of the salt after decomposing the barium malate and tartrate. In establishing the curves, therefore, with known amounts of the two acids, the same excess of ammonium sulfate was used in each case as would be present in determining an unknown.

4. **Reaction of the Medium.**—Yoder[1] found that two equivalents of mineral acid completely destroy the effect of uranyl acetate, that or-

[1] *Loc. cit.*

[2] H. C. Gore, *J. Assoc. Off. Agric. Chemists*, 1, 480–484 (1915).

[3] *Ibid.*, 120–130 (1915).

[4] P. B. Dunbar and R. F. Bacon, "The Determination of Malic Acid," *U. S. Dept. Agric. Bur. Chem. Circ.*, 105 (1912).

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ganic acids had a much slighter effect, and that free alkali disturbed it but little. Walden[1] used four equivalents of potassium hydroxide to overcome the acidity of one equivalent of uranyl nitrate. Gore[2] found that if the malic and tartaric acids are neutralized previous to treatment, higher readings are obtained. He also found that the addition of acetic acid to the neutralized malic and tartaric acids gave higher readings. Two cc. of glacial acetic acid per 100 cc. of solution gave maximum readings with uranium; but with molybdenum 6 cc. of acetic acid are required for malic acid and over 16 cc. for tartaric acid before maximum readings are obtained. No explanations have been offered for this behavior of acetic acid in connection with these uranium and molybdenum complexes. In the present method it was decided to employ 6 cc. of acetic acid per 100 cc. of solution of neutralized acids. This is too much for the maximum uranium readings and too little for the molybdenum; but it is the best average that could be struck. Any divergence from maximum polariscope readings will occur in the curves of knowns and unknowns alike.

5. **Amount of Activator to be Used.**—Yoder[1] found that 1.25 equivalents of uranium for each molecule of malic acid gave the maximum readings. According to Walden's[1] hypothesis that the uranium molecule enters at the hydroxyl group, one equivalent should be sufficient; but even under optimum conditions it never is. With molybdenum 3 molecular equivalents are necessary. The interesting fact of these ratios is that both more and less of the activator than is necessary for maximum readings gives a marked decrease in the reading. This is strikingly shown in Gore's graphs.[2] Therefore, in working with an unknown amount of either organic acid, it is quite impossible to add the correct amount of activator for maximum rotations. Yoder[1] used 0.7 g. uranium acetate in 25 cc. of solution; Dunbar and Bacon[3] in their methods saturate their solutions with powdered uranyl acetate, which usually requires from 2 to 3 g. for 25 cc. of solution. Gore[1] found it easier to employ a standard solution of uranyl acetate and of ammonium molybdate. A solution is also used in the Official Method.[4] It has the advantage of giving a definite amount of salt, and giving it in solution immediately; it requires 2 or 3 hours of shaking to saturate a solution with uranyl acetate, and then the amount that dissolves depends somewhat upon the amount of malic and tartaric acids present. In the present work it was decided to use standard solutions of the two activators, of such strength that 10 cc. will furnish 0.8

[1] *Loc. cit.*

[2] H. C. Gore, Twenty-ninth Meeting of Assoc. Off. Agric. Chemists, *U. S. Dept. Agr. Bull.*, 162, 63–71 (1913).

[3] *U. S. Dept. Agr. Bur. Chem. Circ.*, 105, 106 (1912).

[4] *J. Assoc. Off. Agric. Chemists*, 1916.

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g. uranyl acetate and 1.0 g. ammonium molybdate, respectively. This will provide about 1.25 equivalents of uranium and 3 equivalents of molybdenum for 0.2 g. of combined malic and tartaric acids in a 25 cc. aliquot. Thus in all determinations 10 cc. of each of the activating solutions are added to 25 cc. aliquots of acid solution; in some cases it will be above and in some below, the amount required for maximum readings, but the difference will likewise obtain in the curves from known amounts of acids.

6. Amount of Malic and of Tartaric Acid Present.—Gore[1] made the most exact study of the effect of concentration on the specific rotation of the activated acids. He corroborated the previous workers in that the specific rotations of malic acid were practically the same for concentrations up to 2.0 g. per 100 cc. With tartaric, however, the case is different, a marked fall in the specific rotation occurring at lower concentrations. It was this lack of linear relations that led him to abandon the proposition for a quantitative method. In the present method lack of linear relations can be completely ignored, as the curves constructed from known amounts of the two acids in question give the rotations, under established conditions, of all combinations of the two acids up to 0.8 g. of malic acid and 0.6 g. of tartaric acid per 100 cc. Amounts of each acid from 0.1 to 0.6 g. are the most convenient to work with and give the most satisfactory results.

7. Kind of Light.—White light gives slightly higher polariscope readings than sodium light. The writer used the light from a carbon-flame lamp in the construction of the accompanying curves, because it happened to be more convenient. Any light, however, can be used, if each individual using the method standardizes his whole procedure, as is discussed in the paragraph, "Standardization of Conditions."

8. Time of Standing.—The uranium and molybdenum complexes with the organic acids in question undergo a very interesting series of changes in optical activity. Yoder[2] took the polariscope reading as soon as the uranyl acetate was dissolved; he says that standing a few hours has no effect, but several days causes a lowering. Dunbar[3] says that the time to reach a maximum reading increases with higher concentrations of tartaric acid; that for 0.5 g. per 100 cc. the maximum is attained in one hour, and that after this time there is a gradual decrease to a constant after two or three days. He recommends the addition of sodium acetate; although it lowers the reading, it causes the maximum to be reached more quickly, and the reading is then constant. The official method calls for a period of 5 hours, or preferably 10, to elapse before taking the reading. Some trials by the writer showed that the two acids and the two activators behaved rather dissimilarly in their fluctuations of optical

[1] *J. Assoc. Off. Agric. Chemists*, 1, 120–130 (1915).

[2] *Loc. cit.*

[3] *U. S. Dept. Agr. Bur. Chem. Circ.*, 106 (1912).

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activity. Some of the experiments are presented in Table I. Since apparently no period could be chosen which would give the absolute maximum for all combinations of the two acids and the two activators, 3 hours was arbitrarily chosen as the time to elapse between the addition of the activator and the taking of the polariscope reading.

TABLE I.—EFFECT OF TIME OF STANDING ON THE OPTICAL ROTATION OF MALIC AND TARTARIC ACID SOLUTIONS TREATED WITH AMMONIUM MOLYBDATE AND URANYL ACETATE.

Acids present in 100 cc. solution.		Length of time of standing.								
Malic. G.	Tartaric. G.	8 min. V°.	1 hr. V°.	2 hrs. V°.	3 hrs. V°.	5 hrs. V°.	7.5 hrs. V°.	10 hrs. V°.	15 hrs. V°.	27 hrs. V°.
				With ammonium molybdate.						
1.034	1.000	32.0	..	52.00	51.87	..	51.75	51.60	..	..
1.034	1.000	..	..	..	..	..	51.80	51.80	51.70	52.25
1.034	0.900	..	..	..	50.35	..	49.50	49.64	49.70	..
1.034	0.900	..	..	..	..	..	49.55	49.83	49.85	..
1.020	0	..	32.82	31.60	31.50	31.77	..	..	..	..
0.270	0	..	8.01	7.34	..	7.50	..	..	..	..
0	0.980	..	28.63	..	26.80	26.88	..	..	..	..
0	0.200	..	5.31	5.17	..	5.18	..	5.25	..	..
				With uranyl acetate.						
1.034	1.000	—6.90	..	—6.80	—6.71	..	—6.55	..	..	..
1.034	1.000	..	..	..	..	..	—6.55	—6.65	—6.60	—6.55
1.034	0.900	..	..	—7.25	—7.16	..	—7.04	—7.03	..	..
1.034	0.900	..	..	..	..	..	—7.04	—7.14	—7.14	—7.33
0.270	0	..	—4.55	—4.84	..	—4.73	..	—4.94	..	..

9. Effect of Temperature on Polarization.—Yoder[1] states that there is a decrease of 0.03° Ventzke for each increase of 1° C. The temperature can thus vary several degrees either side of 20° without any appreciable effect on the polarization.

10. Effect of Sunlight.—Sunlight appears to have a destructive effect on the acid complexes of uranium,[2] hence the solutions must be kept in the dark before polarizing.

11. Isolation of the Acids.—In order to avoid the presence of as many substances as possible other than malic and tartaric acids, it is necessary to effect a separation of them. Various methods of separating them as the lead or barium salt have been suggested, the most satisfactory of which is the one adopted in the official method for malic acid.[3] The juice is first neutralized with ammonia, in order to prevent crystallization of acid tartrate when alcohol is added. The pectins are then removed by two volumes of alcohol, excess of barium acetate added, and then 95% alcohol up to 14 volumes (about 89%). This gives not only

[1] *Loc. cit.*

[2] Gore, *J. Assoc. Off. Agric. Chemists*, 1, 480–484 (1915).

[3] *Ibid.*, 1 (1916).

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practically complete removal of the malic acid, but also tartaric and citric acids. Hence the latter acid, as mentioned in Section 2, must be absent from the material. A trial by the writer showed that the above procedure separated tartaric acid so completely that the filtrate from the barium tartrate, after evaporation of the alcohol and treatment with uranium and molybdenum in the usual way, gave readings of 0° in the polariscope. Therefore, this procedure is adopted in the present method.

12. Standardization of Conditions.—A perusal of the above eleven sections makes it evident that many factors may affect the rotatory power of solutions of malic and tartaric acids containing uranyl acetate or ammonium molybdate. It is also obvious that the directions, reagents, and conditions used by the writer in the construction of his graphs must be rigidly adhered to by all other users of the method if his rotations are to be duplicated. Some of the reagents and conditions, however, may be difficult to duplicate in some laboratories. Therefore, it is strongly recommended by the writer that each worker adopt conditions and reagents as near as possible to those listed here, and then standardize his procedure against known amounts of malic and tartaric acid. This can best be done by using, say, 0, 0.3 and 0.8 g. per 100 cc. of each acid alone and in combination with a similar series of the other. These 9 determinations, applied to the curves given herein, will indicate the correction to be made on each subsequent polariscope reading on unknown material before using that reading on the graphs. Those factors which are likely to be subject to change in different laboratories, and which can be changed without jeopardizing the method (provided they are incorporated in the above standardization) are as follows: the kind of light used with the polariscope, the length of time of standing before polarizing, the temperature at which the polarization is made, and the purity of the uranium and molybdenum salts (in other words, the amounts of the activating materials used).

Method in Detail.

The following solutions are required: (1) Standard alkali for titration; (2) ammonium hydroxide, approximately normal; (3) glacial acetic acid; (4) ammonium sulfate, 20 g. per 100 cc. of solution; (5) about 10% barium acetate in 50% alcohol; (6) ammonium heptamolybdate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, 10.00 g. per 100 cc. of solution; (7) uranyl acetate, $UO_2(C_2H_3O_2)_2\cdot 2H_2O$, 8.00 g. per 100 cc. Both this compound and the molybdate should be the purest obtainable, and the solutions filtered perfectly clear before using. Heat will aid the solution of the uranyl acetate.

The details of the method follow: Most of them are taken directly from the official method for malic acid, or from the processes worked out by Gore and his associates.

An amount of the sample that, judged by titration or by previous experience, will probably furnish at least 0.1 g. of either acid, and not more

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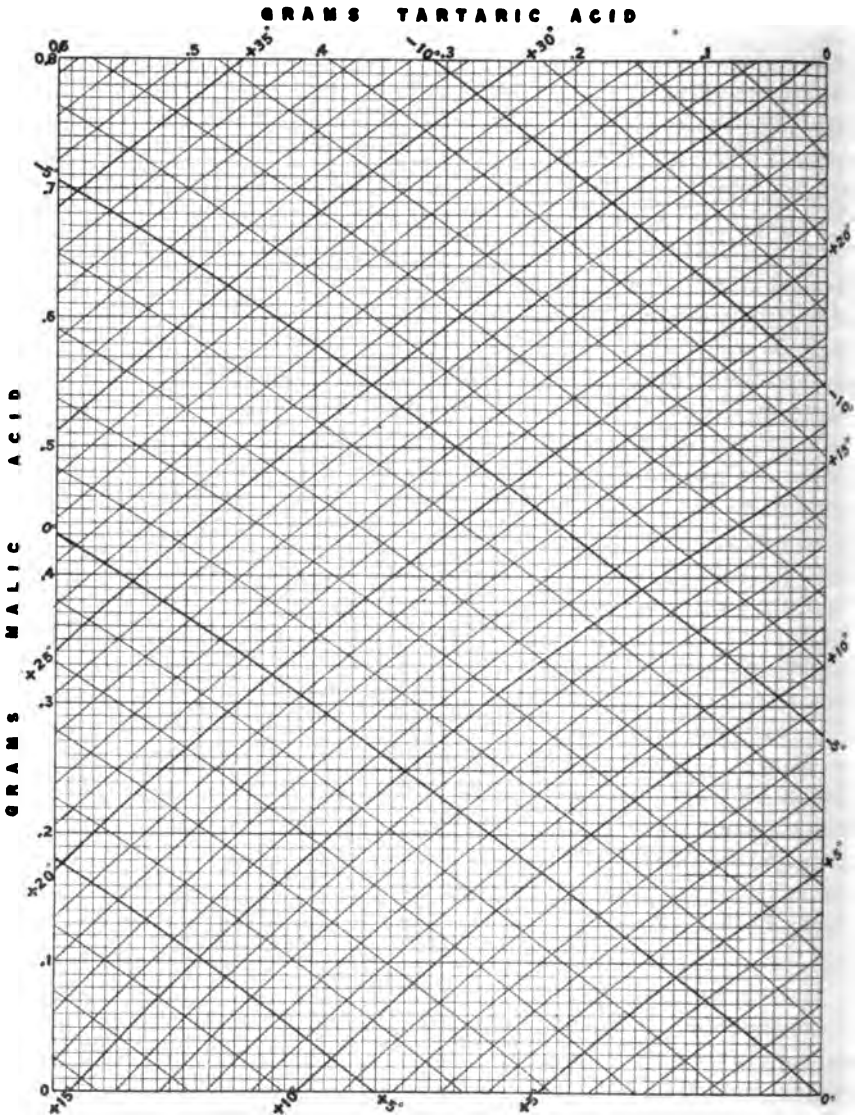

Fig. 1.

Chart for the determination of malic and tartaric acids. The curves which slant down from left to right represent the polariscope readings for combinations of malic and tartaric acids activated by uranyl acetate; the curves which slant up from left to right represent the readings with ammonium heptamolybdate. To ascertain the amount of the two acids present in a solution, obtain the optical activity of the solution as activated by uranyl acetate and ammonium molybdate, according to the prescribed method. Find the point of intersection of the curves representing these two polariscope readings; this point indicates on the abscissas the grams of tartaric acid, and on the ordinates the grams of malic acid, in 100 cc. of the solution polarized. (The original chart was constructed to include 1.0 g. of malic acid and 0.8 g. of tartaric acid. Owing to limited space on the printed page, the above abridged graph is used. The complete curve can be obtained from the author on request.)

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than 0.6 g. of tartaric acid and 0.8 g. of malic acid, is neutralized with the ammonia, treated with 2 volumes of 95% alcohol, the pectins filtered off on a Büchner funnel and washed with alcohol. To the filtrate is slowly added an excess of the barium acetate solution and then enough 95% alcohol to make 14 volumes to 1 of the original solution. The precipitate of barium salts is most easily removed by centrifuging, as they filter with difficulty. If filtration must be employed, it should be done on a Büchner. The precipitate is transferred to a beaker with hot water, heated to boiling, 10.0 cc. of the ammonium sulfate solution slowly added to decompose the barium malate and tartrate; the mixture is concentrated on the steam bath to about 80 cc. volume and transferred to a 100 cc. flask. After cooling, 6 cc. of glacial acetic acid are added and the contents made up to the mark with water. It is then either filtered clear, or, more easily, centrifuged until the supernatant liquid is clear. Two 25.0 cc. aliquots of the perfectly clear solution are treated, respectively, with 10.0 cc. of the uranium acetate, and 10.0 cc. of the ammonium molybdate solution. After standing in the dark for 3 hours the solutions are polarized in a 2 dcm. tube at about 20°. Any dark green color that has been formed by reduced molybdenum can readily be dispelled by a drop of bromine water without appreciably affecting the results. The two readings are then referred to the graph, and the amounts of malic and of tartaric acids are computed according to the directions under the graph.

It was hoped in the beginning that a simple algebraic expression involving the two readings and the quantities of the two acids present could be used to calculate the results. Since the ratios are so far from linear, however, any such equations would necessarily involve also a corrective numerical factor, and this factor would change too frequently to be of use. Since the graph can be read with an accuracy of ±0.003 g. of each acid, this method of calculation brings the results within the limit of experimental error for the rest of the method.

Application of the Method.

The foregoing procedure furnishes a method applicable for all products containing *d*-tartaric acid or *l*-malic acid or both. Citric acid is probably the only interfering acid, and a scheme is in mind whereby this can be allowed for or eliminated. Highly colored solutions can be worked with only after decolorizing with bromine and neutralizing the hydrobromic acid formed with ammonia. This procedure, however, always gives low results.

Table II gives the results of a few trials of the method, and shows what accuracy can be expected. Duplicate determinations agree very well. The recovery of added malic acid is also very satisfactory. Tartaric acid, however, gives more trouble, as ammonium tartrate is much less soluble in alcohol than ammonium malate; and natural products usually

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TABLE II.—ANALYSES OF VARIOUS PRODUCTS FOR MALIC AND TARTARIC ACIDS BY THE PROPOSED METHOD.

No.	Material.	Polarizations. Molybdenum. V°.	Polarizations. Uranium. V°.	Acids found. Malic. G.	Acids found. Tartaric. G.	Added acids recovered. Malic. G.	Added acids recovered. Tartaric. G.
697	25.0 cc. apple juice[1]	+ 8.4	— 4.8	0.272	0.010	...	...
701	25.0 cc. apple juice	+ 8.4	— 4.8	0.272	0.010	...	...
702	25.0 cc. apple juice	+ 8.4	— 4.8	0.272	0.010	...	...
705	25.0 cc. apple juice[2]	+ 7.2	— 4.6	0.250	—0.005[3]	...	...
706	25.0 cc. apple juice	+ 7.5	— 4.7	0.258	—0.004	...	...
709	25.0 cc. apple juice + 0.300 g. malic	+17.4	—10.1	0.560	0.010	0.304	...
710	25.0 cc. apple juice + 0.300 g. malic	+17.4	—10.1	0.560	0.010	0.304	...
711	Extract of 200 g. sugar beet[4]	0.0	0.0	0	0	...	...
712	Extract of 200 g. sugar beet	0.0	0.0	0	0	...	...
721	25.0 cc. apple juice[5]	5.0	— 2.8	0.166	0.012	...	...
722	25.0 cc. apple juice	+ 5.0	— 2.9	0.170	0.010	...	...
726	25.0 cc. apple juice + 0.300 g. malic	+14.4	— 8.2	0.460	0.010	0.292	...
727	25.0 cc. Armour's grape juice[6]	+ 5.0	+ 0.2	0.088	0.125	...	...
728	25.0 cc. Armour's grape juice	+ 5.4	+ 0.2	0.088	0.133	...	...
729	25.0 cc. Armour's grape juice + 0.500 g. malic	+18.9	— 7.8	0.530	0.125	0.442	...
730	25.0 cc. Armour's grape juice + 0.500 g. malic	+19.3	— 8.0	0.541	0.126	0.453	...
731	25.0 cc. apple juice[7]	+ 3.8	— 1.9	0.120	0.020	...	...
732	25.0 cc. apple juice	+ 3.8	— 2.2	0.126	0.012	...	...
733	25.0 cc. apple juice + 0.300 g. tartaric	+10.5	+ 1.4	0.136	0.280	...	0.264

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734	25.0 cc. apple juice + 0.300 g. tartaric.....	+10.5	+ 1.4	0.136	0.280	...	0.264
735	25.0 cc. apple juice + 0.800 g. tartaric.....	+22.9	+ 8.1	0.123	0.755	...	0.739
736	25.0 cc. apple juice + 0.800 g. tartaric.....	+ 4.0	— 1.2	0.108	0.050	...	0.034[8]
737	25.0 cc. apple juice[9].....	+ 6.8	— 4.0	0.226	0.006	...	...
738	25.0 cc. apple juice.....	+ 6.6	— 3.8	0.219	0.005	...	...
739	25.0 cc. apple juice + 0.800 g. malic.....	+29.2[10]	—17.0	1.040	0.005	0.815	...
740	25.0 cc. apple juice + 0.800 g. malic.....	+29.2[10]	—17.0	1.040	0.005	0.815	...
741	25.0 cc. apple juice + 0.800 g. tartaric.....	+26.3	+ 6.0	0.230	0.770	...	0.765
742	25.0 cc. apple juice + 0.800 g. tartaric.....	+ 8.2	— 2.1	0.204	0.106	...	0.100[8]
743	25.0 cc. apple juice + 0.200 g. tartaric.....	+11.4	— 1.4	0.230	0.200	...	0.195
744	25.0 cc. apple juice + 0.200 g. tartaric.....	+11.4	— 1.4	0.230	0.200	...	0.195

[1] Wealthy apples; titre of the 25.0 cc. was 37.0 cc. 0.1 *N* alkali, equivalent to 0.248 g. malic acid.

[2] Another batch of Wealthy apples; titre of 25.0 cc. was 34.3 cc. 0.1 *N* alkali, equivalent to 0.230 g. malic acid.

[3] The intersection of the two curves in the graph fell outside the chart.

[4] Titre of the sample was 15.4 cc. 0.1 *N* alkali. The acids of beets are oxalic and citric.

[5] Baldwin apples, titre of the 25.0 cc. was 21.2 cc. 0.1 *N* alkali, equivalent to 0.142 g malic acid.

[6] Titre of 25.0 cc. (using the natural indicator of the juice) was 30.5 cc. 0.1 *N* alkali, equivalent to 0.228 g. tartaric acid. Decolorized with bromine after neutralizing with ammonia.

[7] Titre of the sample was 14.2 cc. 0.1 *N* alkali, equivalent to 0.095 g. malic acid.

[8] Tartaric acid crystallized out from the acetic acid solution; it apparently lowers the malic acid value also in some way.

[9] Titre of the 25.0 cc. was 29.0 cc. 0.1 *N* alkali, equivalent to 0.194 g. malic acid.

[10] Due to an error in the amount of ammonium molybdate solution added to these, the readings are low, and the intersection of the curves on the graph falls considerably outside the chart. Assuming the uranium reading to be correct, and that there is 0.005 g. tartaric acid involved, the intersection of these two lines in the graph gives a value for malic acid of 1.040 g., which is very close to the expected amount.

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contain sufficient potassium to cause the precipitation of acid tartrate when large amounts of tartaric acid are involved in an analysis. Working with purified acids, the curves were constructed for amounts of tartaric acid up to 1.0 g.; they are published through 0.8 g. only, however, since that is the limit of use in practice.

The qualitative composition of a material to be analyzed should be known since results are sometimes open to question when the point of intersection on the graph falls close to one side. As an example of this, it will be noticed that in Nos. 705 and 706, the data indicate an apparently negative amount of tartaric acid, whereas Nos. 709 and 710, from the same batch of juice, show tartaric to be present.

Although the method is not yet everything that could be desired, nevertheless it is believed that it does constitute an easy and fairly reliable means of assaying these two acids when occurring singly or together.

ST. PAUL, MINNESOTA.

[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, HARVARD UNIVERSITY.]

THE CONFIGURATIONS OF ORGANIC COMPOUNDS AND THEIR RELATION TO CHEMICAL AND PHYSICAL PROPERTIES.

BY ARTHUR MICHAEL.

Received January 30, 1918.

The experimental proof[1] that in the addition of halhydric acids and halogens to acids of the acetylene series, and in the reverse elimination reactions, trans-processes are favored, showed that the then adopted configurations of all stereomeric substances, excepting those given by van't Hoff to the dibasic, unsaturated acids, had to be reversed, as they had been based on the Wislicenus hypothesis of the occurrence of cis-processes.[2] In the new classification a more marked connection between the energy-content and many of the physical properties could be traced, although certain groups of stereomers showed anomalous properties.[3] Since then, there has been very little progress made in this direction; indeed, recently, Pfeiffer[4] stated that *a priori:* "It is hardly possible to decide from the configuration which of the stereomers has the higher melting point, or represents the more stable modification."

It will be shown that it is possible to coördinate these relations and to explain the apparent exceptions, but it should be emphasized that van't

[1] Michael, *J. prakt. Chem.*, [2] **52**, 289 (1895).

[2] *Ibid.*, 359–365. The configurations given by Pfeiffer (*Z. physik. Chem.*, **48**, 55–62 (1904)), which were based on my experimental results, were not new, as is sometimes stated in text books and papers, but were a repetition of those given in my paper (*Ibid.*, 363).

[3] Michael, *Ibid.*, 345; *Ber.*, **34**, 3644, footnote 4 (1901).

[4] *Z. physik. Chem.*, **48**, 57 (1904).

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Hoff's first theorem, which presupposes a radical difference in the spacial relations of the axial carbons and in the nature of their rotation, in saturated and unsaturated substances, has been not only experimentally disproven,[1] but all the reasons advanced in its favor are untenable.[2] This conclusion follows, too, from the second law of thermodynamics, since in every organic molecule a rotation about a common carbon axis must take place if thereby an increase of entropy will result, and its free energy is able to overcome the hindrance to the change. The extent of this hindrance, which represents the stability of the stereomer, is, primarily, the bound energy of the carbon atoms at the axis, and that existing spacially between the atoms directly or indirectly joined to them. After this entropic status has been established, no further rotation is possible as long as the energy conditions remain unchanged. This condition does not imply, however, that the atoms are then static; indeed, it is absolutely necessary to assume that they are all in a more or less condition of vigorous oscillation, although in a restricted sphere.[3]

The ability of unsaturated stereomers and the corresponding saturated substances to rotate is simply one of degree.[1] In the latter group the advent of a relatively slight physical or chemical force may cause such a change, and it is due to this slight hindrance that, excepting comparatively restricted groups of bodies, saturated derivatives exist in only one modification.

According to Wunderlich[4] a carbon atom may be a homogenous sphere with four equal segments, where chemical union with other atoms takes place. A simpler hypothesis, and the most probable spacial conception, is to accept, with Werner,[5] a sphere as the form and connect it with the view of the writer,[6] that, in removing an atom from each of two adjacent radicals in an organic, saturated substance, part of the energy thus liberated appears as free chemical energy at the unsaturated carbons, and part goes to increase the bound energy between these carbons and, spacially, between all the atoms joined to them; and, also, with the view of Richards[7] that atoms are compressible by chemical force.

The energy and the affinity relations of a carbon, which is joined to three atoms or groups, evidently depend on their chemical nature; if the relations are such that it may unite with the unsaturated carbon in a

[1] Michael, *J. prakt. Chem.*, [2] **46**, 425 (1892).

[2] Michael, *Ann.*, **390**, 39 (1912).

[3] Otherwise, it is not possible to explain the fact that atoms may stand in practically the same spacial relation to two or more other atoms in the molecule.

[4] "Konfiguration organischer Moleküle," 1886, see, also, Auwers, "Entw. der Stereochemie," 1890, pp. 18–35.

[5] *Lehrb. d. Stereochemie*, pp. 15, 186 (1904).

[6] *J. prakt. Chem.*, [2] **60**, 298 (1899).

[7] THIS JOURNAL, **36**, 2417 (1914).

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similar radical,[1] then part of the free energy in these carbons will be changed into bound energy and heat, and the same energy transformation will take place spacially between the atoms or groups joined to them. In this conversion of free into bound energy these carbon spheres are compressed together to form a segment, the size of which depends on the magnitude of the energy changes that occur between the carbons and spacially between the atoms of the groups joined to them. This segmentation of the axial carbons should be less in cis- than in trans-succinic acid for two reasons: First, the negative energy of the carboxyls is less neutralized by the nuclear hydrogens; in consequence, the axial carbons are relatively more negative and have, therefore, less affinity for each other. Secondly, the smaller conversion, spacially, of the free energy in the atoms joined to the axial carbons.

Since unsaturation is accompanied by an increase in the bound energy at the axial carbons, the extent of their segmentation, must be greater in unsaturated than in the corresponding saturated stereomers; while the free energy of the axial carbons must be greater in the maleinoid than in the fumaroid form, the extent of the segmentation must be smaller. In the act of unsaturation, therefore, not only do the masses of the axial carbons become condensed, but the spacial distance becomes less between all atoms in cis-positions joined to them.

Further, the energy necessary to cause a rotation of atoms or groups about the axial carbons must be far less in saturated than in the corresponding unsaturated derivatives, and in the latter bodies less for the maleinoid than for the fumaroid forms.

The principal points of accumulation of the free energy in stereomeric, unsaturated acids, are at the unsaturated carbons, carbonyl and hydroxyl groups; and its extent, as manifest in their atoms, depends on their direct and spacial relations to the other atoms in the molecules. Evidently, the relative values of the sum total of the free energy in all the atoms of such stereomers are in a direct relation to those of their heats of combustion, and, as Stohmann[2] has shown that these factors and the affinity constants of simple stereomeric derivatives of acrylic acid are in a direct relationship, the latter values in such acids must stand in a direct proportion to the total free energy.[3] This connection justifies classifying these stereomeric acids as maleinoid or fumaroid on the basis of the magnitude of their affinity constants.

The classification refers, however, only to the proportion of the total free energy in the stereomers, and it does not necessarily follow that the

[1] THIS JOURNAL, 32, 996 (1910).

[2] *J. prakt. Chem.*, [2] 40, 357 (1889); 46, 530 (1892).

[3] Michael, *Amer. Chem. J.*, 39, 2 (1908); Michael and Bunge, *Ber.*, 41, 2907 (1908).

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relations, as shown at the acidic hydrogens, represent, also, the relative values of all the other atoms in the molecules.

Acetylenic linkage, as a further development of double, brings the carbon spheres in contact over a larger segment than in the corresponding ethylenic configuration, and causes an augmentation of the free energy at the axial carbons, with a further spacial juxtaposition of the atomic groups. In this class only one, the cis-derivative, exists, owing to the great difference between it and a trans-form in the energy of the two systems.[1]

Butyric acid may exist in the stereostructures:[2]

I. $(CH_3)H_2C - CH_2(COOH)$. II. $CH_3(H)HC - CH_2(COOH)$.

Owing to the slight hindrance to rotation in saturated, monobasic acids the free acid should have the stereoform representing the maximum intramolecular, atomic neutralization, and, therefore, the smaller affinity constant. With a base, the system should endeavor to realize the maximum increase of entropy, and the acid should assume the more acidic configuration, provided the difference between the heats of neutralization of the two forms by the base is sufficient to overcome the slight hindrance to rotation. Essentially the same relation arises in the behavior of butyric acid toward the relatively basic water, and the affinity constant of the acid represents, therefore, the value of the more acidic stereo-

[1] The free energy in CH_2, when introduced in a fatty hydrocarbon without change in saturation, is largely transformed into bound energy and heat, and the latter is dissipated. On the other hand, when two such radicals unite, a much larger proportion of their free energy remains unchanged and, as less heat is lost, the thermic value of CH_2 must be greater in ethylene than in a saturated hydrocarbon. Acetylene, often miscalled a "spontaneously decomposable" substance, is unstable only in the sense of reactivity, due to the great free energy in the system. Its formation at a high temperature from so many organic bodies, conforms with the general tendency under such conditions to form systems with greater content of free energy; it is then stable to a high temperature (*c.* 1300°), when the heat-energy overcomes the bound energy between the carbons and hydrogens, and it passes over into the towards heat more stable system of hydrogen and a highly polymerized carbon. Misleading, too, is its classification as an endothermic body; it is so only in reference to a very complex form of carbon, which would be formed from a diatomic modification with a tremendous conversion of free into bound energy and heat. Strictly speaking, endothermic and exothermic should only be used when the thermic values are obtained from reactions where the molecular conditions before and after the chemical change are comparable, or, when allowance may be made for differences. A revision of thermochemical data from this point of view would be of great help in disentangling the present confusion.

[2] This word, and stereoform, are suggested as synonyms for configuration. To represent spacial formulas, whenever it is possible, in a single line, atoms or groups in cis-position will be inclosed in parentheses, and the axial carbons denoted by a hyphen or hyphens. In some cases, it may be desirable to use asterisks, instead of parentheses, to indicate the cis-relation; and, with saturated compounds, to use the two methods simultaneously.

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structure, while a solution of the acid in greater concentration may contain a mixture of the two configurations.

Bruni[1] has shown that organic substances with similar configurations form isomorphous mixtures, and that free butyric acid stands in this relation to crotonic acid; that is, it is the fum. form.[2] The anomalous rise of the affinity constants in passing from propionic (1.34)[3] to butyric acid (1.5), has been explained[4] by the negative $\overset{6}{C}$ of the introduced $\overset{6}{C}\overset{7}{H_3}$ being spacially much nearer to $\overset{1}{H}$ than the $\overset{7}{H_3}$. In trans-$\overset{6}{C}\overset{7}{H_3}$ the spacial relations of the elements are reversed, and, in consequence, the replacement of trans-$\overset{6}{H}$ by $\overset{6}{C}\overset{7}{H_3}$ invariably lowers the affinity constant, which for trans-butyric acid, if it could exist in dilute aqueous solution, would be less than that of propionic acid, probably about 1.2. Owing to the much greater hindrance to rotation in unsaturated compounds, crotonic acid exists free in two forms:

$$\text{(I).}\ (CH_3)HC = CH(COOH). \quad \text{(II).}\ CH_3(H)C = CH(COOH).$$

These configurations may be derived from that of acrylic acid (5.6) by cis- or trans-replacement of $\overset{6}{H}$ by $\overset{6}{C}\overset{7}{H_3}$, and the effect on the affinity constant must be to increase or to lower the value. The constant of crotonic acid (2) shows that it has the fumaroid configuration (II), which agrees, as will be shown, with all the physical and chemical properties of the acid.

It is generally accepted that the replacement of an atom or a group in a stereomeric substance does not lead to a relative change in the order of the configuration. As this conclusion follows directly from the present mechanical stereochemical theory, and as it has been a fruitful source of confusion, it is of importance to show that it is erroneous.

For this purpose, we shall consider the configurations of the chlorocrotonic acids in relation to their affinity constants and their properties.

[1] *Gazz. chim. ital.*, [2] **34**, 495 (1905).

[2] Probably, at ordinary temperature, the free acid represents a dynamic mixture of many fum. and few mal. configurations, and the proportion of the latter should increase with heat increment; at the boiling point the relative relations may be reversed.

[3] All of the affinity constants in this paper should be multiplied by 10^{-5} to obtain the absolute values.

[4] Michael, *J. prakt. Chem.*, [2] **60**, 335 (1899). The "Scale of Combined Influence" —2, 3, 5, 6, 4, 7 (9, 10, 11), 8—*Ibid.*, 331; THIS JOURNAL, **32**, 999 (1910); **34**, 849 (1912)) was first derived from the affinity constants of saturated, monobasic acids and applies, therefore, only to atoms in cis-positions. $\overset{1}{H}$ always signifies the acidic hydrogen in this paper.

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α-Acids:

(I). $(\overset{*}{C}H_3)HC = CCl(\overset{*}{C}OOH)$, K 158. (II). $CH_3(H)\overset{*}{C} = CCl(\overset{*}{C}OOH)$, K 72.

β-Acids:

(III). $(\overset{*}{C}H_3)ClC = CH(\overset{*}{C}OOH)$, K 9.5.

(IV). $CH_3(\overset{*}{C}l)C = CH(\overset{*}{C}OOH)$, K 14.4.

Configuration (I) is derived from that of allocrotonic acid (6–7)[1] and (II) from that of crotonic acid (2). The effect of chlorine in the fifth position to the acidic hydrogen is clearly shown by the enormous increase in the values of the constants. And the much greater value of (I) is due, primarily, that in it the halogen is in the unimportant fourth place to the positive β-H, while in (II) it is in the very important fifth position to three such atoms; and, secondarily, that it is a derivative of allocrotonic acid. In agreement with the affinity constants and the energy relations, is the conversion of α-chloroallocrotonic (I) into α-chlorocrotonic acid (II) by heat or by mineral acids, and all the other physical properties of these compounds.

In the α-halogen crotonic acids the usual relations between the affinity constants and physical properties prevail, but in the β-acids they are largely reversed; for instance, the higher melting acid (94°) is more soluble and has the larger constant (14.4). Notwithstanding, it yields crotonic acid on reduction and goes over on heating into the lower melting form (60°). The derivative represented by configuration (III) is derived from that of allocrotonic acid, which is a factor in favor of a larger affinity constant, but in it the halogen is in the trans-position to $\overset{1}{H}$, and in the cis-position to α-H, while in IV it is in the cis- to $\overset{1}{H}$ and in the trans-place to α-H. The negative energy of the Cl in (III) is, therefore, not only used up more than in (IV), but it influences the acidic hydrogen to a much less extent, and, since Cl has a much greater negative influence than $\overset{6\ 7}{C}H_3$,

[1] Ostwald's value is 3.6, but he used a preparation containing at least 50% of crotonic acid. Michael, *J. prakt. Chem.*, [2] **46**, 236 (1892). It is very desirable that the term "allo" be restricted to its original use (Michael, *Ber.*, **19**, 1384 (1886)), which is to denote the stereomer with the larger energy-content, *i. e.*, the maleinoid form. In this sense, it is far preferable to the term "iso," which is also used to represent structural isomerism. The name of the maleinoid modification may be always formed by prefixing "allo" to that of the fumaroid stereomer, and the energy relations of the compounds are shown with certainty in this way. To express the fact that some fumaroid derivatives form maleinoid addition products, "allo-" has been prefixed to the addendum (Michael, *Ber.*, **34**, 3645 (1901)); thus, cinnamic acid and chlorine in the dark give cinnamic allo-dichloride. Absolutely wrong, is the use of α- and β- to indicate stereoisomerism, when there is a possibility of confusion with the accepted structural use. It is unfortunate, that the suggestion (*Ibid.*, **19**, 1381) to use some contraction for allo has not been adopted.

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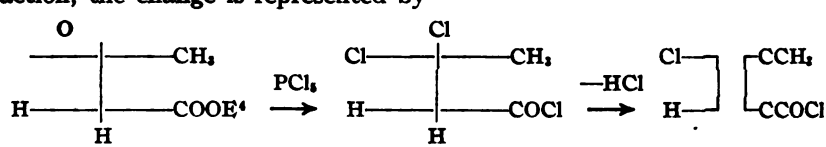
the last two factors outbalance the comparatively slight difference between the affinity constants of the mother acids, and cause the reversion in the relations of the affinity constants. Thereby, the chlorine derivative of the fumaroid crotonic acid becomes, in its energy relation, maleinoid to the stereoacid and *vice versa*.

The reason of the inversion of the usual melting-point relations in these acids to their energy-contents is now obvious. The increase by replacing H by Cl is 23° larger in the trans- (III) than in the cis-β-substance (IV); but this difference is considerably less than that between the melting points of the two crotonic acids (57°). We can now understand the greater solubility of the higher melting acid in water, as this property is directly connected with the larger content of free chemical energy; also, that it gives the lower melting, fumaroid form on heating, and crotonic acid on reduction.

In accordance with the above classification and the tendency to trans-addition, is the formation of the higher melting, β-chlorocrotonic acid (IV) from tetrolic and hydrochloric acids.[1]

These relations between configurations and affinity constants explain, also, the apparently anomalous results obtained in the reduction of the acids. The lower melting β-chlorocrontoic acid (9.5), as a derivative of allocrotonic acid, should give that acid exclusively, but it yields a mixture containing the fumaroid form in a larger proportion. The energy accompanying the formation of nascent hydrogen suffices to the partial conversion, which would be still greater if the acid had a larger affinity constant, and thus generate a greater intramolecular heat of reaction.[2] This interpretation is confirmed by the reduction of the lower melting α-chloro-acid (158), which should also yield allocrotonic acid, as here the conversion into crotonic acid is practically complete.[3]

β-Chloroallocrotonic acid (III) is formed in the action of phosphorus pentachloride on acetoacetic ester, a reaction which is accompanied by the elimination of HCl and the conversion of the carbethoxyl into the acid chloride group. Free acetoacetic ester, as a saturated derivative, has the stereostructure with the maximum intramolecular atomic neutralization; assuming the trans-elimination of HCl from the first product of the reaction, the change is represented by



[1] Friedrich, *Ann.*, **219**, 370 (1883).

[2] Wohl, *Ber.*, **40**, 2290 (1907).

[3] Michael, *J. prakt. Chem.*, [2] **46**, 266 (1892).

[4] The writer suggests the utmost abbreviation, compatible with clearness, in

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The formation of β-chloroallocrotonic acid, by trans-elimination of HCl, from allocrotonic dichloride also agrees with the above interpretation.

With the tautomerization of acetoacetic ester, and similar derivatives, the possibility of stereomers arises.

(I). $H_3C(HO)C = CH(COOE)$. (II). $(H_3C)HOC = CH(COOE)$.

The problem, which of these stereoforms is mal., depends on the relative influence of β-CH_3 and β-OH, and may be answered by the effect of these radicals on the affinity constants of propionic acid. In passing from that acid to (cis) butyric acid the value rises 0.25–0.3, while to (cis) β-hydroxy-propionic acid the increase is 1.7. Evidently, $\overset{6\ 7}{\text{cis-OH}}$, in comparison to $\overset{6\ 7}{\text{cis-CH}_3}$, is decidedly negative in its action on $\overset{1}{H}$ and, as the stereomeric relations of acids passes over to the esters, stereostructure (I) must represent the mal. form. The difference in the values of hydroxyl and methyl, however, is considerably less than between chlorine and methyl, in the same positions, which makes it probable that (I) would be easier convertible into (II) than allo-β-chlorocrotonic acid is into β-chloroallocrotonic acid; indeed, enol-acetoacetic ester may consist of a mixture in which the fum. form (II) predominates.

Stereo enol-acetoacetic esters are, as yet, unknown but their *O*-methyl derivatives probably exist. Friedrich[1] obtained by the action of sodium

designating organic radicals. Thus, instead of the clumsy Me and Et, etc., the first letter of the alkyl radical should be used. No ambiguity would occur up to the 12th series, except in hexyl and heptyl which could be represented by Hx and Hp, and to denote the alkylenes and alkines, e and i could be used as suffixes. Atoms or radicals, prefixed or suffixed, to the above abbreviations could indicate substitutions of hydrogen, respectively, additions, and could be used, too, in connection with the Geneva nomenclature. Thus, BH and Bi-2 would represent butane and butine-2, and 2.3-Cl_2- AH or Ae-Cl_2-(2.3) would stand for 2.3-dichlorpentane or amylene-(2.3)-dichloride.

To curtail the names of acid radicals by suffixing c in the same way would lead to confusion, owing to the use of Ac for acetyl, and to the names of some of the acids in higher series; it would be preferable to start from Ac as acetyl and form formulas in the way given above; thus, P-AcCl would denote butyryl chloride. In designating aldehydes and acids, the Geneva nomenclature, in connection with the hydrocarbon contractions, could be used.

Further, a similar curtailment in designating the various classes of organic derivatives; thus, instead of iso-, sec-, tert-, quart-, keto-, stereomeric, it would be equally significant to use i-, s-, t-, q-, k-, st-. The employment of Ph for phenyl could be usefully extended to Tl, Xl, Npl, etc., for tolyl, xylyl, naphthyl, etc., and e and i, used as suffixes, to characterize further unsaturation; thus, $Phe(NH_2)_2$ would denote phenylenediamine.

These suggestions are regarded as tentative and can doubtlessly be much improved. Some system of this sort would, after a short experience, convey a quicker and more definite impression of the chemical nature of the compound, especially when of a complicated structure, than the one in present use.

[1] *Ann.*, 219, 322 (1883).

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ethylate on both β-chlorocrotonates, in the heat, the same β-ethoxycrotonate.[1] Later, Enke[2] got a β-methoxycrotonic ethyl ester by the action of sodium methylate on β-chloroallocrotonic ester, and v. Pechmann[3] an *O*-methyl derivative by the action of diazomethane on acetoacetic ester. The latter product showed a higher boiling point, but on saponification with alkali it yielded the same β-methoxycrotonic acid. Von Pechmann called this product "β-methoxy-cis-crotonic ester" and gave it the configuration $(CH_3)H_3COC = CH(COOE)$. Apart from the fact, that the separate existence of these bodies seems still open to question, owing to the unusually facile stereomerization of the acid by the alkali, this stereostructure cannot be correct. $\overset{6\ 7}{CH_3}$ is decidedly positive to $\overset{6\ 7\ 8}{OCH_3}$ in its influence on $\overset{1}{H}$, and the mal. configuration is $H_3C(H_3CO)C = CH(COOE)$. This grouping agrees with the higher boiling point, as a derivative of (trans) crotonic ester, and with the instability of the corresponding acid; it is in accord with the formation of Friedrich's ethoxycrotonic ester, by the action of HCl on a mixture of alcohol and acetoacetic ester,[4] which proceeds with the preliminary addition of alcohol to the keto-carbonyl, and then by trans-elimination of water and shifting of the α-hydrogen.

$$EO(\overset{*}{CH_3})(HO)C - CH_2(\overset{*}{C}OOE) \longrightarrow (CH_3)EOC = CH(COOE).$$

Stereomeric thio-derivatives have been obtained by Autenrieth[5] in the action of sodium ethylmercaptide, and sodium phenylsulfinite, on the β-chlorocrotonates. Accepting direct substitution, and the Wislicenus configurations, the stereostructures $(CH_3)ES$, or $PhSO_2$, $C = CH(COOH)$ were given to the higher melting, more soluble products obtained from allo-β-chlorocrotonic acid (94°). As $PhSO_2$ is a very strong negative radical, and ES- much more so than EO-, the mal. forms must be $H_3C(ES$, or $PhSO_2)C = CH(COOH)$, and products of these stereostructures must be formed as the result of an addition and then elimination process in the reactions. This classification agrees with all the chemical properties of these substances; for instance, the silver salt of the fum. β-thioethoxycrotonic acid[6] splits off Ag_2S more readily than the stereomic salt, which is characteristic of the trans-relation,[7] and the mal. phenylsulfon-acid is converted by heat into the fum. modifi-

[1] An explanation will be given under substitution in the second communication.
[2] *Ann.*, **256**, 209 (1890).
[3] *Ber.*, **28**, 1627 (1895).
[4] Curtiss, *Amer. Chem. J.*, **17**, 438 (1895).
[5] *Ann.*, **254**, 222 (1889); **259**, 332 (1890); *Ber.*, **30**, 1629 (1895).
[6] Wrongly called thioethyl-crotonic acid.
[7] Michael, *J. prakt. Chem.*, [2] **52**, 311, 326 (1895).

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cation. Escales and Baumann[1] prepared β-dithiophenoxy-butyric ester, by condensation of phenyl mercaptane and acetoacetic ester, which with alkali loses phenyl mercaptane, and gives the mal. β-thiophenoxycrotonate. Accepting saponification as the first step, the salt thus formed should be a derivative of the more acidic configuration, *i. e.*, H_3C, $PhS(\overset{*}{P}hS)C - CH_2(\overset{*}{C}OONa)$, which, with loss of PhSH, should give the salt of the more acidic, mal. stereoacid.

The second law of thermodynamics demands that in all addition processes the chemical system should strive to realize the maximum increase of entropy, *i. e.*, the formation of the fumaroid product, but the conditions with stereomeric derivatives are far more complicated than in ordinary reactions: first, because the reagent may act catalytically, before or coincident with the addition, and convert completely or to a more or less extent, the maleinoid into the fumaroid form; and, secondly, because of the undoubted existence in all unsaturated, organic derivatives of a powerful force that tends to cause trans-additions. This directive trans-force, which finds no expression in our present stereochemical theory,[2] involves a hindrance, since an intramolecular shifting of atoms or groups, or their gyration about the axial carbons, must take place, which the system must have sufficient energy to overcome in order to permit trans-addition.

Phenylpropiolic acid gives by the mild action of molecular hydrogen a mixture of the maleinoid cinnamic acids, that is, the reaction proceeds by cis-addition, because the system has not sufficient free energy to cause the shifting or gyration. But the fumaroid cinnamic acid is formed through the extra energy accompanying the formation of nascent hydrogen. On the other hand, molecular hydrogen and acetylene dicarboxylic acid, whose content in free energy finds expression in an affinity constant about that of sulfuric acid, would, probably, yield fumaric acid.

Evidently, the use of addenda with large content of free energy should favor trans-addition, which, indeed, takes place in all additions of halhydric to acetylenic acids; that the latter bodies with bromine give mixtures of the stereomeric addition products, in which the compounds formed in the trans-process predominate, is undoubtedly connected with the decreasing difference between the energy-contents of the mono-, and di-halogen derivatives. For instance, if the α-H of $H_3C(Cl)C = CH(COOH)$, and that of $(H_3C)ClC = CH(COOH)$, is replaced by Cl, the relative difference between the affinity constants should decrease in the new acids, for, in

[1] *Ber.*, 19, 1790 (1886); Autenrieth, *Loc. cit.*

[2] Pfeiffer's attempt (*Z. physik. Chem.*, 48, 40 (1904)) to explain trans-additions, by an inherently improbable assumption, failed, for, apart from various other reasons, cis-additions also take place, and such processes are incompatible with his hypothesis.

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the first instance, the α-Cl is in the cis-place to $\overset{5}{H_3}$, while, in the other case, it is cis only to the comparatively, subordinate $\overset{4}{H}$. Since α-Cl has a great influence on the acidic hydrogen, its effect to increase the constant must be greater in the latter than in the first substitution.

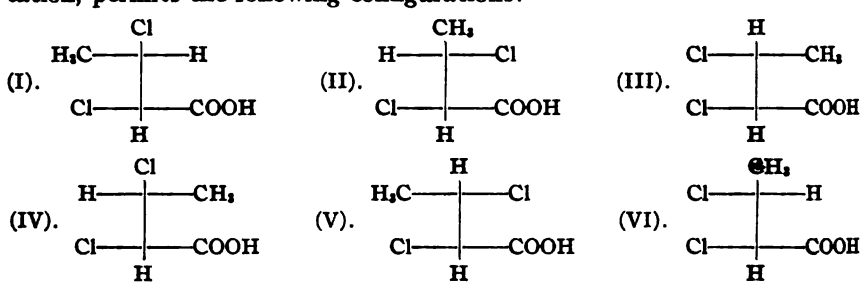
The same directive trans-force prevails in additions to ethylenic derivatives. For instance, Werner[1] assumed the trans-process in the addition of bromine to maleic acid, to explain the close chemical relationship between the addition product and racemic acid. This assumption conforms not only to the energy-conditions, and the molecular rotary power of the isoamyl esters,[2] but the racemic nature of the dibromo acid has recently been experimentally proven.[3]

In the addition of bromine to tetrolic acid a mixture of the stereomeric dibromides are formed,[4] in which the lower melting form is found in larger proportion. Trans- and cis-additions give the following configurations:

(I). $CH_3(Br)C = CBr(COOH)$. (II). $(CH_3)BrC = CBr(COOH)$

By trans-addition, evidently, the more acidic, maleinoid bromo acid (I) is formed, and this lower melting (94°) and more soluble form, loses bromine by trans-elimination[5] more readily than the higher melting, fumaroid acid[6] (120°), and is converted into it by the action of hydrobromic acid.[7]

Trans-addition of chlorine to crotonic and allocrotonic acids and rotation, permits the following configurations:[8]



[1] *Lehrb. d. Stereochemie*, 226 (1904).

[2] Michael, *Amer. Chem. J.*, **39**, 15 (1908).

[3] McKenzie, *Chem. Soc.*, **101**, 1196 (1911); Holmberg, *Svensk Kem. Tidskr.*, No. 5 (1911).

[4] Michael, *Ber.*, **34**, 4221 (1901).

[5] The former rule, IX (Michael, *J. prakt. Chem.*, [2] **52**, 346 (1895)) that a fum. halogen acid loses halogen, or halhydric acid, easier than the corresponding mal. form should be changed to trans- taking place more readily than cis-elimination.

[6] Michael and Mighill, *Ber.*, **34**, 4225 (1901).

[7] Pinner, *Ibid.*, **28**, 1877 (1895).

[8] With cis-additions these configurations are reversed, *i. e.*, (I), (II) and (III) result from allocrotonic acid, and (IV), (V) and (VI) from crotonic acid. The α-H offers the least hindrance to migration (Michael, *J. prakt. Chem.*, [2] **60**, 361 and 368 (1899)).

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The most acidic of these stereomers should be (II) and (V), since in them chlorine is in the cis-position to the acidic hydrogens; further, (II) should be more acidic than (V), because in the latter chlorine is cis to $\overset{4}{C}H_3$, while in the former it is cis to $\overset{4}{H}$. Since in such saturated derivatives the affinity constants represent the most acidic of the possible configurations, it is evident that the determination of the constants of the stereomeric crotonic dichlorides should decide the nature of the additive process. It has been shown[1] that the constant of the dichloride from crotonic acid (820) is larger than that from allocrotonic acid (607), and it follows from these values that the addition is a trans-process.

The configuration of allocrotonic dichloride given above is confirmed by the formation from α-chlorocrotonic acid.[2]

$$H_3C(H)C = CCl(COOH) \xrightarrow{\text{trans HCl}} (CH_3)(\overset{*}{C}l)HC - CH(Cl)(\overset{*}{C}OOH)\ (V).$$

Tiglic and Angelic Acids.

The substitution of $\overset{5}{H}$ by $\overset{5}{C}H_3$ in a fatty acid invariably proceeds with reduction of the K value; accordingly, in tiglic (I) and angelic (II), or allotiglic acids,

$$(I).\ H_3C(H)C = CCH_3(COOH).\quad (II).\ (CH_3)HC = CCH_3(COOH)$$

which are formed in this way from crotonic and allocrotonic acids, there is a decrease from 2 and 6–7 to 0.9 and 5.[3]

In agreement with the configurations are all the physical and chemical properties of these stereomers. Interesting is their behavior towards bromine in the dark and in sunlight. In the dark they yield separate dibromides; in sunlight, tiglic acid gives the same dibromide as in the dark, and also a small amount of angelic dibromide, while angelic acid also yields to a greater or less extent, according to conditions, tiglic dibromide with angelic dibromide.[4]

The configuration relations in the trans-addition of bromine to these acids are similar to those discussed above in the addition of chlorine to the crotonic acids. The behavior of angelic acid towards bromine may now be explained; in the dark, the energy in the "polymolecule" of halogen and acid is insufficient to convert it into tiglic acid, but with the assistance of actinic, or of heat energy, stereomerization proceeds the addition to a more or less extent.

[1] Michael and Bunge, *Ber.*, **41**, 2909 (1908).

[2] Michael and Schulthess, *J. prakt. Chem.*, [2] **46**, 259 (1892).

[3] The greater proportionate decrease in tiglic acid (I) is probably due to the fact that the energy in CH_3 is used up to a larger extent by being cis to CH_3 than to H.

[4] Fittig, *Ann.*, **259**, 29 (1890); **273**, 127 (1893); J. Wislicenus, *Ann.*, **272**, 7 (1893); **274**, 99 (1893).

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Trans-elimination of HBr from tiglic and angelic dibromides leads, whether by migration of CH_3 or Br, to the following stereoforms:

(I). $(CH_3)BrC = CCH_3(COOH)$. (II). $H_3C(Br)C = CCH_3(COOH)$

Although angelic dibromide yields a bromo derivative (II) of (fum.) tiglic acid, it evidently represents the mal. modification and, accordingly, it is more soluble in water than bromoangelic acid (I). Its melting point (101°) is slightly higher than that of the latter acid (95°). Crotonic acid melts 57° higher than allocrotonic acid, and the introduction of Cl in the cis-, respectively, in the trans-position to COOH, reduces the difference to 34°, respectively, 23°. When the much smaller difference in the melting points of tiglic (65°) and angelic (45°) acids is taken into consideration, it is evident that the slight difference between that of bromoangelic and bromotiglic acids might have been expected. These configurations of the bromo acids are confirmed by the behavior of the potassium salts at 100°, since only that of bromoangelic acid (I) decomposes easily into butine-2 and CO_2, which agrees with the trans-position of Br and COOK.[1]

Influence of Ethylenic Unsaturation on Affinity Constants.

This subject has been investigated recently by Fichter and Pfister,[2] who find that the values for α,β,Δ-aliphatic acids are only slightly higher, indeed in the pentenic series, less, than those of the corresponding saturated derivatives, and that they increase in the β,γ,Δ-acids to fall with further removal of the unsaturation from the carboxyl group. They compare these relations with the great increase in the introduction of halogen in the α- and then the progressive decrease in the β- and γ-positions, and conclude that double linkage cannot be considered a negative substituent, although in other groups of derivatives it apparently acts as such.[3]

The effect of the above unsaturation is to increase the affinity constant in three ways: First, it removes basic hydrogen; secondly, the axial carbons and the atoms or groups joined to them become relatively more negative or less positive, and, finally, the unsaturated, axial carbons and the atoms in cis-position to carboxyl, spacially approach the acidic hydrogen. The large increase in the affinity constant with such unsaturation follows from these relations; also, that the difference between the values of two homologous, saturated acids is always less than those of the corresponding ethylenic acids with similar configurations.

To explain the experimental observations with these acids, it is necessary to assume that the hydrogen unsaturation of a carbon increases the

[1] Michael, *J. prakt. Chem.*, [2] **52**, 311 (1895).

[2] *Ann.*, **334**, 201 (1904).

[3] See Henrich, *Theorien Org. Chem.*, **1912**, pp. 83–103. For a criticism of the views of Henrich and Vorlaender on this subject, and for interpretations founded on the energy and affinity relations, see Michael, *J. prakt. Chem.*, [2] **68**, 496 (1903); THIS JOURNAL, **32**, 1002 (1910).

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constant much more than the removal of a hydrogen in the same position as the carbon to $\overset{1}{H}$. The great increase in the affinity constants accompanying unsaturation makes such an assumption very probable; for instance, the presence of two, completely unsaturated carbons in the fifth position to the acidic hydrogens of acetylene dicarboxylic acid, coupled with the spacial approachment of the carboxyls, give it approximately the acidity of sulfuric acid.[1]

The supposed contradictions in the negative influence of the ethylenic bond are partly due to the comparison of the values of dissimilar configurations. Although the constant of the fum. crotonic acid (2) is only slightly higher than that of (cis) butyric acid (1.5), the much larger value of the really comparable (cis) allocrotonic acid (6–7) plainly shows the very considerable negative influence of the unsaturated radical.[2] It is, also, not permissible to conclude, with Fichter, from the constants of crotonic (2) and vinylacetic (3.8) acids that β,γ- has a greater effect than α,β-unsaturation, since a comparison of the value of the latter acid with that of allocrotonic acid (6–7) leads to exactly the opposite conclusion. The true relations appear to be that such a β,γ,Δ-derivative has a larger value than the isomeric α,β-acid of the trans-, but smaller than that of the cis-series. With trans-β,γ- and γ,δ-pentenic acids, omitting the atoms common in each group, we have the following relations to $\overset{1}{H}$:

$$\beta,\gamma:\quad \Delta\overset{5}{C} + \text{trans-}\overset{7}{C} + \text{cis-}\overset{7}{H} + \text{trans-}\overset{8}{H_2}$$

$$\gamma,\delta:\quad \overset{5}{C} + \Delta\text{-}\overset{7}{C} + \text{cis-}\overset{8}{H} + \overset{7}{H} + \overset{7}{H}$$

The influence of the carbons and of the cis-hydrogen evidently favors the acidity constant of the β,γ-acid, while the remaining hydrogens act in the opposite direction; but, with the relatively greater influence of the carbons, it is evident that it should possess the larger constant.

With α,β-pentenic acid stereoisomerism is possible and the one known substance is fum., since the constant (1.5) is less than that of crotonic acid, and a reduction of the value is only possible by substitution of trans-$\overset{7}{H}$ by $\overset{7}{C}\overset{8}{H_3}$.

Fichter has called attention to an apparent anomoly in this series in that the constant of the α,β-acid (1.5) is less than that of the corresponding saturated acid (1.6). This unusual relation is the result of a comparison of acids with unlike configurations. In the change from (cis) butyric

[1] Ostwald, *Z. phys. Chem.*, 3, 382 (1889).

[2] The decided negative influence is also apparent in the values of the comparable propionic (1.3) and acrylic (5.6) acids.

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(1.52) to (cis) valeric acid (1.59)[1] the replacement of a cis-$\overset{7}{H}$ by $\overset{7}{C}\overset{8}{H_3}$ increases the constant slightly, while from (trans) crotonic (2) to (trans) α,β-pentenic acid a decrease takes place. The cis-form of α,β-pentenic acid, whose stereostructure is like that of valeric acid in dilute solution, would show a much larger constant, probably 7–8.

The only known β,γ-pentenic acid also represents a fum. substance, as it may be derived from vinylacetic acid (3.8), and shows a smaller constant (3.3). Comparing the α,β- and β,γ-acids, as shown above, leads to the following relations:

$$\alpha,\beta:\quad \Delta\overset{4}{C} + \text{trans-}\overset{6}{C} + \text{trans-}\overset{7}{H_2} + \text{cis-}\overset{6}{H}$$

$$\beta,\gamma:\quad \Delta\overset{6}{C} + \overset{4}{C} + \overset{5}{H} + \overset{6}{H} + \text{cis-}\overset{7}{H}$$

In the β,γ-acid the carbon atoms exert a decidedly greater negative, cis-$\overset{7}{H}$, in place of cis-$\overset{6}{H}$ a less positive, and $\overset{5}{H} + \overset{6}{H}$ a positive, but evidently a smaller effect. In this series, the β,γ-acid has, therefore, the larger constant.

The constants of the acids in the hexenic series are

$$\alpha,\beta\text{- (1.9)};\quad \beta,\gamma\text{- (2.6)};\quad \gamma,\delta\text{- (1.7)};\quad \delta,\epsilon\text{- (1.9)}.$$

All these values are higher than that of the saturated capronic acid (1.4). The comparatively low values of the first three acids show that they are fum. modifications, and the relations of their constants to each other agree with the explanations given above for the corresponding pentenic acids.

A striking anomaly is shown in that α,β-pentenic acid (1.5) has a smaller constant than α,β-hexenic acid (1.9), that is, the introduction of trans-$\overset{8}{C}\overset{9}{H_3}$ has an effect opposite to that of $\overset{6}{C}\overset{7}{H_3}$ and $\overset{7}{C}\overset{8}{H_3}$ in the trans-relation. This rise cannot be explained by assuming a cis-configuration for the hexenic acid, since its value would be considerably higher than that of the acid in question. It seems probable, that it is due to a periodicity in the spacial positions of atoms in trans-positions, like there

[1] These are the values given by Franke (*Z. physik. Chem.*, **16**, 480 (1895)), who used acids prepared by fractionation from "Kahlbaum's" purest products. It is unfortunate that physical chemists are under the delusion that really pure preparations can be separated in that way from products that are evidently mixtures. Billitzer (*Monatsh.*, **20**, 666 (1899)) obtained his valeric acid (1.61) through malonic ester, but we know now that it is impossible to completely separate the mono- from the dialkyl malonic derivatives, except by chemical means (Michael, *J. prakt. Chem.*, [2] **72**, 537; *Ber.*, **38**, 2093 (1905)). The determinations of standard affinity constants would give data of great theoretical importance; Ostwald's values were obtained largely from more or less impure acids. These remarks unfortunately apply to the majority of physico-chemical, organic investigations.

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is in cis-positions; and, that trans-$\overset{8}{C}$ is spacially nearer to $\overset{1}{H}$ than trans-$\overset{9}{H}$, *i. e.*, its effect is comparable to that of cis-$\overset{6\,7}{CH_3}$. This increase, in connection with the decrease in passing from valeric to capronic acid, explains why the constant of α,β-hexenic acid is higher than the corresponding (cis) saturated acid, instead of being lower, as in the fifth series.

The substitution of α-H in α,β-pentenic acid (1.5) by methyl introduces $\overset{5\,6}{CH_3}$ and reduces the constant to 1, which is approximately the same percentage as in the analogous change from acetic to propionic acid. The further conversion to butyric acid (1.54) brings in the negative $\overset{6\,7}{CH_3}$, and, analogously, the change from α-methyl- to α-ethyl-pentenic acid causes an increase (2). An exception occurs in that the introduction of α-$\overset{6\,7}{CH_3}$ in β,γ-pentenic acid (3.3) reduces the constant to 3, while the larger value of the α-ethyl derivative (3.4) agrees with theory; as does, that α-$\overset{7\,8}{CH_3}$ introduced into γ,δ-pentenic acid causes only a very slight change. The most marked discrepancies from theory are shown by the acids formed in the substitution of cis-$\overset{6}{H}$ in α,β-pentenic acid by $\overset{6\,7}{CH_3}$, and in the β,γ-derivative, of cis-$\overset{7}{H}$ by that radical, when the constants are lowered, instead of increased.[1]

Dibasic Unsaturated Acids.[2]

Ostwald[3] determined the constants of maleic and fumaric acids and their methyl derivatives and found that the value of mesaconic (K_1 79) is somewhat less than that of fumaric (K_1 93), while that of citraconic (K_1 340) is only about one-third of that of maleic (K_1 1170) acid. Since the methyl group reduces the constant, and is nearer to carboxyl in mesaconic than in citraconic acid, Ostwald expected that the relative changes in the relations would be reversed. In this problem, the primary factors are the positions of the introduced atoms to

[1] Fichter and Mueller, *Ann.*, 348, 258 (1906).

[2] The hindrance to rotation in succinic acid should be greater than in monobasic, saturated acids, and it probably exists mainly in the trans-form in solution. This conclusion agrees with the small affinity constant (K_1 6.6), which, for the cis-acid, should not be less than K_1 25. Bruni's observation, that succinic and fumaric methyl esters have similar (trans) stereostructures also confirms this conclusion, as esterification represents a partial neutralization of the negative, acidic energy and, unless there is a decided hindrance to rotation, the succinic ester should assume the maleinoid configuration. This relative stability of the fum. succinic acid is connected with the properties of the stereomeric alkyl derivatives, a subject which will be discussed in a later paper.

[3] *Z. physik. Chem.*, 3, 383 (1889).

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the acidic hydrogens and the oxygens; the indirect influence of the latter atoms on the change in the affinity constant is, evidently, much greater when the carboxyls are in cis-, than in trans-position. When the new influences coincide in their effect, then there should be a decided difference, otherwise, they should neutralize each other to a more or less extent and the change should be relatively much smaller. The replacement of trans-$\overset{6}{H}$ by CH_3 in maleic acid introduces trans-$\overset{6\,7}{CH_3}$ to one of the acidic hydrogens and $\overset{5\,6}{CH_3}$ to the other. Each change reduces the negative energy of the acidic hydrogens and, also, that of the oxygens, which, owing to their being in cis-position to each other, is a considerable factor in the great decrease.

That the primary constant of fumaric acid (93) is so much less than that of maleic acid (1170) is due to the much greater reduction of the negative energy of the oxygens by hydrogen in the cis-, than in trans-position; further, to the trans-relationship of these oxygens and, finally, that the Δ-carbons are less negative. The values for bromofumaric (K_1 1800) and bromomaleic acid (K_1 7000)[1] lie much closer together, which is due to the replacement of a H by an atom that, for spacial reasons, increases the negative energy at the acidic hydrogen of the fum. body to a far greater extent than it does in the mal. derivative. Corresponding energy changes occur with the further substitution of H by halogen.[2]

Ethyl-maleic acid may be derived from citraconic acid by replacing a trans-H of the methyl group by CH_3, which introduces $\overset{6\,7}{CH_3}$ and trans-$\overset{7\,8}{CH_3}$ to the acidic hydrogens, and $\overset{5\,6}{CH_3}$ and trans-$\overset{6\,7}{CH_3}$ to the oxygens. $\overset{6\,7}{CH_3}$ increases the constant somewhat, but trans-$\overset{7\,8}{CH_3}$ causes a greater decrease, which is enhanced by the same influence on the oxygens. The K_1 constant falls from 340 to 238.

The corresponding change in mesaconic acid introduces $\overset{6\,7}{CH_3}$ and cis-$\overset{7\,8}{CH_3}$ to the acidic hydrogens and $\overset{5\,6}{CH_3}$ and cis-$\overset{6\,7}{CH_3}$ to the oxygens. $\overset{6\,7}{CH_3}$, also, probably, cis-$\overset{7\,8}{CH_3}$, increase the constant; $\overset{5\,6}{CH_3}$ reduces the negative energy of the oxygens, which is offset by cis-$\overset{6\,7}{CH_3}$. As, with trans-carboxyls, the latter influences are subordinate and the (K_1) value increases methylfumaric acid (79 to 94). The change from ethyl-, to propyl-mesaconic acid brings in $\overset{7\,8}{CH_3}$ and cis-$\overset{8\,9}{CH_3}$; these influences are similar to those in passing

[1] Holmberg, *J. prakt. Chem.*, [2] **84**, 162 (1911). The smaller value of dibromomaleic acid (K_1 3700) indicates that it exists partly as anhydride in dilute aqueous solution.

[2] Walden, *Z. physik. Chem.*, **8**, 479 (1891); Holmberg, *Loc. cit.*, p. 166.

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from butyric to valeric and from valeric to capronic acids, where a very slight increase and slightly greater decrease occur. The value (K_1) falls from 94 to 93.

Cinnamic Acids.

That the stereomeric relations in the cinnamic series are closely related to those in the crotonic was proven experimentally,[1] and the attempt of J. Wislicenus[2] to change this relationship was afterwards abandoned.[3] All the properties of cinnamic (3.5) and allocinnamic (14.2) acids conform with the configurations

$$\text{(I) } C_6H_5(H)C = CH(COOH). \quad \text{(II) } (C_6H_5)HC = CH(COOH)$$

and the affinity constants show that C_6H_5 is decidedly negative to H in the cis-position, but positive to it in the trans-place. Cinnamic acid and Cl_2 in the dark,[4] or in light free from actinic rays,[5] yields the mal. dichloride (84°); in sunlight, the high-melting (163°) fum. product.[6] These results are comparable, and the configurations are similar to those discussed above with crotonic acid, only, owing to the characteristic greater hindrance to stereomerization in the latter series, actinic sunlight not cause such a change, which may be effected, however, by heating crotonic allodichloride with HCl.[7] Unfortunately, the stereomeric cinnamic dichlorides decompose somewhat into chlorostyrols in dilute solution, so that a determination of their affinity constants is impossible,[8] but it follows conclusively from other properties, that the lower melting dichloride is the mal. acid; *i. e.*, its formation from cinnamic acid and, therefore, that of the fum. dichloride from allocinnamic acid,[9] proceed by trans-addition.

In the dark, cinnamic acid and bromine yield the high melting, fum. dibromide (201°) and only 10% of the mal. stereomer (91°), but with the methyl and ethyl esters the proportion of latter products increase to about one-third, respectively, one-half.[10] To effect trans-addition the hindrance due to the shifting of an atom or group has to be overcome, and the decreased yield of allo-addition product with bromine over that with chlorine may be connected with its smaller content of free energy. Further, the increase in allo-product with the esters may be due to the decrease of free energy in the carboxyl accompanying esterization, which should

[1] Michael, *Ber.*, **19**, 1378 and 1384 (1886); **20**, 550 (1887).
[2] *Rauml. Anordnung U. S. W.*, 47 (1887).
[3] *Ibid.*, 2nd edition, 79 (1888).
[4] Liebermann and Finkenbeiner, *Ber.*, **28**, 2235 (1895).
[5] Michael and Smith, *Amer. Chem. J.*, **39**, 16 (1908).
[6] Erlenmeyer, *Ibid.*, **14**, 1867 (1881).
[7] Michael and Bunge, *Ber.*, **41**, 2912 (1908).
[8] *Ibid.*, 2913.
[9] Liebermann and Finkenbeiner, *Ber.*, **28**, 2235 (1895).
[10] Michael and Whitehorne, *Ibid.*, **34**, 3660 (1901); Michael and Smith, *Am. Chem. J.*, **39**, 16 (1908).

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lessen the hindrance to rotation; in agreement, is the increased percentage of allo-dibromide with the ethyl over that with the methyl ester. This explanation is confirmed by the behavior of chlorine and bromine towards other unsaturated derivatives. Bromine unites solely by trans-addition with maleic and fumaric acids; with acetylene dicarboxylic acid, where the hindrance to rotation is increased, also by the cis-process. Crotonic acid and halogens units by trans-addition, but, with tetrolic and bromine, both processes occur simultaneously, while with chlorine apparently only trans-addition takes place.

Bromine and phenylpropiolic acid give a mixture of the stereomeric dibromocinnamic acids.[1]

(I) $(C_6H_5)BrC = CBr(COOH)$. (II) $C_6H_5(Br)C = CBr(COOH)$.

The formation of (II) proceeds by trans-addition and represents the mal. form; as a derivative of cinnamic acid (132°), it has a higher melting point (139°) than the fum. acid (100°), but its mal. character is shown by its conversion by bromine into (I), and the configuration of that acid (I) by its conversion by condensation into dibromindone.[2] Chlorine and phenylpropiolic acid[3] yield a single α,β-dichlorocinnamic acid (120°), which, by its comparatively low melting point, and through its conversion into dichloroindone, is characterized as the fum. derivative (corresponding to (I)). Since bromine, under the conditions of the addition, is able to catalytically convert the mal. (I) into the fum. (II) product, it is not improbable that some of the latter substance is thus formed indirectly. And the abnormal formation of only the fum. dichloride may be due to the chlorine, with its greater energy, entirely stereoisomerizing the first-formed mal. addition product.[4]

The addition of HBr to phenylpropiolic acid yields two β-bromocinnamic acids,[5] melting at 160 and 134°, but it will be shown in a subsequent paper that the lower melting acid is formed secondarily by the catalytic action of the mineral acid on the higher melting stereomer, from which it may also be obtained by heating.[6] The relations, excepting the catalytic transmutation, agree with those of the chlorocrotonic acid formed by trans-addition of HCl to tetrolic acid. Here, too, the mal. character of the higher melting acid is shown in the greater solubility in water, and its high melting point conforms with its derivation from cinnamic acid. On the other hand, a most marked difference exists in the behavior of these bromo acids on

[1] Roser and Haselhoff, *Ann.*, **247**, 138 (1888).

[2] Roser and Haselhoff, *Loc. cit.*

[3] Nissen, *Ber.*, **25**, 2665 (1892).

[4] It would be of interest to study these reactions in the dark.

[5] Stockmeier, Dissertation, p. 73; Michael and Browne, *Ber.*, **19**, 1379 (1886); **20**, 552 (1887).

[6] Erlenmeyer, *Ann.*, **287**, 24 (1895).

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reduction, since the 159° melting β-acid yields allocinnamic acid,[1] whereas, according to its configuration, it should give the fum. acid; also, the ease with which it decomposes into phenyl acetylene, and a smaller velocity of elimination of HBr, are opposed to the stereostructures given above, and to the relation of the corresponding halogen acids in the crotonic series.

An attempt[2] to determine the affinity constants of the β-bromo acids was without success, but those of the corresponding chloro-acids are known.[3] The higher melting acid is the mal. derivative, but its affinity constant (28) is only slightly higher than that of the fum. acid (27.2). This relation shows that the increase in the affinity constant of acrylic acid (5.6) caused by cis-$\overset{6}{Cl}$, less the decrease by trans-$\overset{6}{C}\overset{7}{C_6H_5}$, is only slightly greater than the increase due to cis-$\overset{6}{C}\overset{7}{C_6H_5}$ plus that of trans-$\overset{6}{Cl}$, and the relation is reflected in the approximation of their melting points and solubilities in water. It is remarkable, that the β-chloro- and β-iodo-cinnamic acids, corresponding to 160° melting β-bromo derivative, yield in the same method of reduction cinnamic, instead of allocinnamic acid.[4] No other problem in the field of stereomeric configurations is so perplexing and enigmatical as that of the β-halogen cinnamic acids, and the recent experimental results have added to the difficulties awaiting a satisfactory solution.

In the next paper, the relations between these configurations of unsaturated acids and their other physical and chemical properties will be treated

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

THE PREPARATION OF PHENYLETHYLBARBITURIC ACID.[5]

BY MARY RISING AND JULIUS STIEGLITZ.

Received March 19, 1918.

Phenylethylbarbituric acid is a member of the ureid group of hypnotic drugs, of which diethylbarbituric acid, introduced as "veronal" and now known as "barbital,"[6] is the best known and most important representative. Phenylethylbarbituric acid, "phenylbarbital,"[7] introduced as "luminal,"

[1] Liebermann and Scholz, *Ber.*, **25**, 950 (1892).

[2] Michael and Bunge, *Ibid.*, **41**, 2913 (1908).

[3] Millikin, Dissertation, Leipsic (1890).

[4] Michael and Whitehorne, *Ber.*, **34**, 3659 (1901).

[5] The work reported on in this article will form part of the dissertation to be submitted to the University of Chicago by Miss Rising in part fulfillment of the requirements for the doctorate degree.

[6] The official name of this drug, adopted by the U. S. Federal Trade Commission in the issuance of licenses for its manufacture, is "barbital." The reasons for the adoption of new official names for the licensed drugs and for the recommendation that these names be generally used by chemists and physicians in this country are presented by one of the authors in the *J. Am. Med. Assoc.*, **70**, 536 (1918).

[7] "Phenyl-barbital" is the name for phenylethylbarbituric acid, which will be used in the issuance of licenses for its manufacture in this country.

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is of specific value as a hypnotic and sedative in the treatment of epilepsy, and, therefore, is one of the group of essential synthetic remedies whose manufacture in this country has become a matter of importance in consequence of the war. In order to be in a position to advise and assist any would-be manufacturer with a minimum loss of time, the authors of this paper have studied the synthetic preparation of phenylethylbarbituric acid. Certain improvements in the method studied have suggested themselves and are reported for the benefit of any one preparing to supply this important synthetic.

The method of preparation of phenylethylbarbituric acid, which was investigated, is indicated in the following series of reactions:

(1) Ethyl oxalate is condensed with the ethyl ester of phenylacetic acid by means of sodium ethylate in order to form the sodium salt of the diethylester of oxalyl-phenylacetic acid.[3]

$$C_2H_5O_2C.CO_2C_2H_5 + H_2C(C_6H_5).CO_2C_2H_5 + NaOC_2H_5 \longrightarrow C_2H_5O_2C.C(ONa) : C(C_6H_5).CO_2C_2H_5 + C_2H_5OH. \quad (1)$$

W. Wislicenus,[1] who carried out this reaction, recommended as the condensing agent the use of pure sodium ethylate, which is prepared by the driving off of the excess of alcohol in a stream of inert gas (hydrogen) from a solution of sodium ethylate in ethyl alcohol.

In this stage of the synthesis two modifications have been found desirable. In the first place, one may do away with the laborious preparation of solid sodium ethylate and effect the combination in absolute ether solution by means of sodium wire and a few drops of absolute (ethyl or methyl) alcohol. A quantitative yield of the desired sodium salt is easily obtained. In the second place, the methyl esters may be substituted for the ethyl esters. Methyl oxalate is a solid and much more easily prepared than the ethyl ester, especially by the method finally adopted by us. The condensation of the methyl esters is, if anything, more smoothly effected than that of the ethyl esters.

(2) In the next stage of the synthesis, the dimethyl oxalylphenylacetic ester is converted by heat into the methyl ester of phenyl malonic acid by the loss of carbon monoxide, according to the method used by Wislicenus on the ethyl ester.

$$CH_3O_2C.CO.CH(C_6H_5)CO_2CH_3 \longrightarrow CO + C_6H_5CH(CO_2CH_3)_2. \quad (2)$$

Here too an advantage in the use of the methyl ester was observed in as much as methyl phenylmalonate is a solid which may be easily purified by recrystallization, whereas the ethyl ester is a liquid, which tends to decompose when distilled, even *in vacuo*.

(3) The ethylation of phenylmalonic methyl ester in alcoholic solution according to

[1] *Ber.*, **27**, 1092 (1894); *Ann.*, **246**, 315 (1888).

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$$C_6H_5CH(CO_2CH_3)_2 + NaOC_2H_5 + C_2H_5I \longrightarrow (C_6H_5)(C_2H_5)C(CO_2CH_3)_2 + NaI + HOC_2H_5 \quad (3)$$

leads to not altogether satisfactory yields as a result of saponification and decomposition of the ester in a parallel reaction, exactly as observed by Wislicenus for the ethyl ester.[1] But again the new methyl ester had the advantage of being a solid, which may be purified by recrystallization. The sodium salt of phenylmalonic methyl ester is easily prepared in ether suspension by treatment of the ester dissolved in absolute ether with sodium wire and a little alcohol. Ethylation of this salt in sealed tubes at 100° has been studied in the hope of improving the yield by avoiding the loss due to the saponifying action of sodium ethylate in alcoholic solution. The results thus far obtained have not been as satisfactory as expected but the effort will be continued, especially in the direction of experiments to be carried out at higher temperatures. The use of an autoclave would be easily compensated for by a greater yield of the ethylated product.

(4) The condensation of ethylphenylmalonic dimethylester with urea is the last stage in the synthesis of phenyl barbituric acid.

$$(C_6H_5)(C_2H_5)C(COOCH_3)_2 + CO(NH_2)_2 \longrightarrow (C_6H_5)(C_2H_5)\underbrace{C.CONHCONH.CO}. \quad (4)$$

According to the patent specifications[2] the condensation is effected by sodium ethylate in alcoholic solution by the heating of the mixture under a reflux condenser. This produced phenylethylbarbituric acid but only in exceedingly small quantity. A far better result was obtained by the method of condensation that Fischer[3] used in the preparation of diethylbarbituric acid, with the modification that sodium methylate in methyl alcohol was substituted for sodium ethylate in ethyl alcohol solution.

Further work on the improvement of the yields in the later stages of the synthesis of phenylethylbarbituric acid is in progress and other methods of accomplishing the synthesis especially with the aid of the Grignard reaction, are to be investigated.

Experimental Part.

1. **Phenylacetic Methyl Ester,** $C_6H_5CH_2CO_2CH_3$.—Phenylacetic methyl ester was prepared in general according to the directions of Wislicenus[4] for the preparation of the ethyl ester. To 200 g. of absolute methyl alcohol are added 100 g. of benzyl cyanide and 20 g. of water. The flask containing this mixture is placed under reflux, and dry hydrogen chloride gas passed into it at a rather rapid rate. The solution becomes hot, and after the gas is passed in for half an hour or so, a heavy white precipitate

[1] *Ber.*, **28**, 815 (1895).
[2] U. S. Pat. 1,025,872 (1912).
[3] *Ann.*, **335**, 338 (1904).
[4] *Ibid.*, **296**, 361 (1896).

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of ammonium chloride settles out with a rather violent reaction. The treatment with hydrogen chloride is continued to saturation, first without cooling, and then the mixture is cooled and saturated in the cold. The flask and contents are left standing for twenty-four hours, and are then heated for one hour on the water bath. The mixture is cooled, and 300 g. of ether and finally just sufficient water are added to it to dissolve the ammonium chloride when shaken in a separatory funnel. The ether solution is separated and washed with 10 cc. portions of sodium carbonate until the washings are alkaline. All the wash waters are combined, including that containing the ammonium chloride, and shaken with a little ether. This ether layer is separated, and all the ether solutions are combined, filtered, and dried over granulated calcium chloride. The oil remaining after the evaporation of the ether is fractionated. The yield of oil of boiling point[1] 212–216° (uncorr.) was 110 g., or 85.9% of the theoretical yield.

In this process, care was taken to wash the ether solution of the oil with only small amounts of sodium carbonate, in order to avoid hydrolysis of the ester by alkali. The alkali was then separated quickly and completely from the ether solution of the ester.

The course of the reaction may be summarized as follows:

Main reaction: $C_6H_5.CH_2.CN + CH_3OH + HCl \longrightarrow C_6H_5CH_2C(:NH_2Cl)OCH_3$ (5)

$C_6H_5.CH_2C(:NH_2Cl)OCH_3 + H_2O \longrightarrow NH_4Cl + C_6H_5.CH_2.CO_2CH_3$ (6)

By reactions: $C_6H_5.CH_2.CO_2CH_3 + HOH \longrightarrow C_6H_5.CH_2CO_2H + CH_3OH$ (7)

and, to some extent: $C_6H_5CH_2C(:NH_2Cl)(OCH_3) \longrightarrow C_6H_5CH_2CONH_2 + CH_3Cl$ (8)

2. Methyl Oxalate, $(COOCH_3)_2$.—Vanino's[2] method for the preparation of methyl oxalate was modified and the following far simpler method used with better results. In Vanino's method the sodium carbonate used rapidly saponifies the ester, lowering the yield.

To 378 cc. of absolute methyl alcohol are added 300 g. of dehydrated oxalic acid. The dehydration is accomplished sufficiently by the heating of the hydrated acid in shallow vessels in a steam oven overnight. The solution of oxalic acid in methyl alcohol is placed under reflux, and hydrogen chloride gas is passed into it in a strong stream. The mixture quickly becomes hot; it is then cooled in an ice bath to prevent decomposition of the ester. White crystals of methyl oxalate separate out slowly after hydrogen chloride has been passed in for some time and a solid mass of

[1] Radziozewski, *Ber.*, 2, 208 (1869), gives the b. p. 220° for the ester prepared from phenylacetic acid in the usual way.

[2] *Präparative Chemie*, 2, 110 (1914).

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crystals eventually forms in the flask. The flask and contents are left standing for twenty-four hours, and the crystals are then brought on a funnel, and kept over suction for some hours to remove the hydrogen chloride. By drying the crystals further *in vacuo* for several days over sodium hydroxide or lime, the last traces of hydrogen chloride are removed. The melting point of the crystals was found to be 53.5°. The yield was 333 g., or 84% of the theoretical yield. This yield includes 28 g. recovered from the mother liquor when cooled to —15°.

Anschütz and Pictet's method,[1] used in the preparation of tartaric acid esters, and said to give quantitative yields for oxalic acid esters, was also tried. It gave very poor results and proved much more laborious than the above method.

3. Sodium Oxalylphenylacetic Methyl Ester, $CH_3O_2C.C(ONa):C(C_6H_5)CO_2CH_3$.—Wislicenus[2] obtained an 85% yield of the sodium salt of oxalylphenylacetic ethyl ester by the condensation of ethyl oxalate with phenylacetic ethyl ester, using alcohol-free sodium ethylate prepared in a stream of hydrogen as the condensing agent. We applied the Nef method of preparation of acetoacetic ester to this condensation, using sodium wire in an ether solution of the two esters, and adding a few drops of absolute methyl alcohol to start the reaction. Our yield ranged from 85 to 92% of the theoretical.

To 80 g. of sodium dried ether are added 4 g. of sodium wire and 20 g. of methyl oxalate. The oxalate dissolves only partially. There are then added 25 g. of phenylacetic methyl ester, and about ten drops of absolute methyl alcohol, and the mixture is placed at once under reflux. Soon after the alcohol is added, yellow crystals begin to form upon the sodium wire, and a flocculent precipitate appears in the ether solution. The sodium dissolves very slowly, with the evolution of hydrogen, and a mass of yellow precipitate gathers in the bottom of the flask, the liquid above it turning to a dark red. Two days are allowed for the completion of the reaction, and the mixture is then heated for one hour on the water bath. It sometimes happened that gentle heating on an electric oven was necessary to start the reaction, and then the precipitate came down rapidly. After the contents of the flask are cooled, the yellow precipitate of sodium oxalylphenylacetic methyl ester is brought upon a filter, washed with dry ether, and dried *in vacuo*. The yield varies from 37 to 40 g.

As the salt is very easily decomposed the product of the reaction must be kept dry. Our product was yellow, and perhaps not absolutely pure but attempts to purify it by solution of the salt in alcohol and precipitation with ether, as recommended by Wislicenus for the corresponding salt of

[1] *Ber.*, 13, 1178 (1880).
[2] *Ibid.*, 27, 1092 (1894).

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the ethyl ester, failed, as the substance turned quickly to a soft, jelly-like mass.

A sodium determination showed that the salt is rather pure.

Subst. 0.7881; Na_2SO_4, 0.1919.
$C_{12}H_{11}O_5Na$. Calc. Na: 8.92%. Found: 8.77%.

The reaction is

$$(COOCH_3)_2 + C_6H_5CH_2CO_2CH_3 + NaOCH_3 \longrightarrow CH_3O_2C.C(ONa) : C(C_6H_5)CO_2CH_3 + 2CH_3OH. \quad (9)$$

4. Oxalylphenylacetic Methyl Ester, $CH_3O_2C.CO.CH(C_6H_5)CO_2CH_3$.—The sodium salt of oxalylphenylacetic methyl ester is treated with cold dilute sulfuric acid in excess, whereby an oil is formed. The oil is separated from the acid by extraction with ether, and the ether extract dried over calcium chloride.

After the evaporation of the ether, the ester is decomposed with the loss of carbon monoxide by being treated *in vacuo* in the manner described by Wislicenus[1] for the ethyl ester. The ester when warmed at 90° C. and 10 mm. shows evidence of decomposition, with evolution of a gas, and change of color of the oil from bright red to dark brown. The manometer shows a decided increase in pressure, and the bubbles of gas forming at the outlet of the pump may be ignited and burn with the blue flame characteristic of carbon monoxide. When the loss of carbon monoxide is complete, the pressure falls rapidly to the original 10 mm. The reaction is expressed in Equation 2 above.

5. Phenylmalonic Methyl Ester, $(CH_3OOC)_2CHC_6H_5$.—The distillation *in vacuo* is continued as described in (4), until the thermometer rises to 130°. The small fraction of impure ester passing over below this point is collected separately. At 120° crystals of phenylmalonic methyl ester form at the tip of the water condenser and in the receiving vessel, and at this time the distillation is interrupted, and the liquid in the flask transferred to an Anschütz distilling flask. The distillation is then resumed, after the pressure is again brought to 10 mm., and the main fraction of the oil distilling between 147° and 159° is collected. This entire distillate crystallizes readily.

The purification of the ester is accomplished by recrystallization from ligroin of low boiling point (40–50°) from which rosets of white crystals separate, when the solvent is allowed to evaporate spontaneously. The melting point of pure crystals was found to be 50°. The ester was identified by analysis.[2]

Subs. 0.1555; CO_2, 0.3628; H_2O, 0.0813.
Calc. for $C_{11}H_{12}O_4$: C, 63.46%; H, 5.82%. Found: C, 63.64%; H, 5.85%.

[1] *Ber.*, **27**, 1091 (1894).

[2] We are indebted to Mr. R. Q. Brewster for this combustion and for the others reported on in this paper.

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The crude yield from 78 g. of the sodium salt of oxalylphenylacetic ester was 42.2 g., or 67% of the theoretical yield.

6. Phenylethylmalonic Methyl Ester, $(CH_3OOC)_2C(C_2H_5)(C_6H_5)$.—Wislicenus[1] describes the alkylation of phenylmalonic ethyl ester with methyl iodide in the presence of sodium methylate. He reports a yield of the pure ester, an oil, which was 60% of the theoretical. Our experience with the ethylation of the methyl ester by the method of Wislicenus (described in detail for malonic esters by Conrad and Limpach),[2] was discouraging with regard to yields, which were very low.

Sodium methylate is prepared from 30 g. of absolute methyl alcohol and 3 g. of sodium. To this solution, 30 g. of phenylmalonic methyl ester are added, and the flask containing the mixture is placed under reflux. After solution of the ester, which occurs readily, 30 g. of ethyl iodide are added in small portions through the condenser tube. There is no apparent reaction, and it is necessary to heat the mixture for three or four days over a water bath in order to bring about the ethylation. That the reaction does not go to completion is shown by the fact that the mixture in the flask remains alkaline. It was, therefore, necessary to neutralize it before proceeding further with the preparation of the ester.

At this point the directions of Conrad and Limpach were modified, with good results. The residue left in the flask after being heated for several days is made neutral, or slightly acid, with dilute sulfuric acid, and enough water is added to dissolve the sodium iodide formed in the reaction, and to cause the ethylated ester to separate in an oily layer at the bottom of the flask. This oil is separated from the water above it, and dried over calcium chloride. The aqueous layer contains a small amount of the oil, and is extracted twice with ether, and the ether solution is dried over calcium chloride. After the evaporation of the ether, the remaining oil, which is dark red in color, is added to the main portion, and distilled *in vacuo*.

From 80 to 90°, at 10 mm., there is obtained a dark red oil and some purple iodine fumes are formed. This change is complete below 100°, and a pale yellow liquid remains in the distilling flask. From 100 to 135°, a fraction of impure ethylated ester is obtained, and from 135 to 155°, the main fraction of the oil distils.

The fraction of the higher boiling point crystallizes when cooled, and remains solid at room temperature. The fraction of the lower boiling point crystallizes slowly on cooling, but softens somewhat at room temperature. The yield of the two fractions before purification was 26 g. or 76% of the theoretical, and the crystals showed a melting point of 33°.

[1] *Ber.*, **28**, 815 (1895).
[2] *Ann.*, **204**, 129 (1880).

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By recrystallization from ligroin of low boiling point, crystals were obtained with a melting point of 37°. The crystals obtained by spontaneous evaporation of the solvent were large, colorless, and transparent.

The ethylated ester was identified by analysis:

Subs. 0.1544; CO_2, 0.3750; H_2O, 0.0954.
Calc. for $C_{12}H_{16}O_4$: C, 66.17; H, 6.83. Found: C, 66.24; H, 6.91.

The reaction is expressed in Equation 3 above.

7. **Phenylethylbarbituric Acid,** $(C_6H_5)(C_2H_5)C.CONHCONHCO$.—The condensation of the phenylethylmalonic methyl ester with urea to form phenylethylbarbituric acid was first attempted by the method described in the patents. The ester and urea are heated under reflux for six hours, with sodium alcoholate as the condensing agent. By the use of this method, we obtained only a very small amount of phenylethylbarbituric acid, and the yield was too low to warrant the use of the method for practical purposes.

The method of Fischer[1] for the preparation of diethylbarbituric acid, was followed next, with much better success and when carried out on a large scale, this method would undoubtedly give a higher yield than was obtained by us in working with small amounts of material.

Sodium methylate is prepared from 14.2 g. of absolute methyl alcohol and 0.9 g. of sodium. To it are added 2.5 g. of phenylethylmalonic methyl ester and 1.1 g. of urea. This mixture is heated in a sealed tube at 105–108°, for six hours. When the tube has cooled, the white precipitate (chiefly of sodium carbonate) is removed and the filtrate is again heated in a sealed tube for six hours at 105–108°. Any further precipitate of sodium carbonate which has formed during the second heating is removed as before. The filtrate, which is alkaline, is neutralized with acetic acid, and the alcohol evaporated *in vacuo*. When the last of the alcohol is gone, the residue in the distilling flask has an oily appearance, and when a few cubic centimeters of water are added, a cloudy emulsion of the oil and water forms. This emulsion is now extracted with ether, and the ether allowed to evaporate spontaneously. The residue is a mass of crystals in a thick oil, and is a mixture of phenylethylbarbituric acid and unchanged ester. It is extracted with ligroin of low boiling point, which dissolves the ester. The remaining white mass is purified by recrystallization from boiling water, and after two recrystallizations, the product shows a melting point of 174°. The crystals are pure white, and lustrous. The yield was close to a gram or about 40% of the theoretical. The reaction is given in Equation 4 above.

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[1] *Ann.*, **335**, 338 (1904).

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NEW BOOK.

A Class Book of Organic Chemistry. By J. B. COHEN, PH.D., B.Sc., F.R.S., University of Leeds. First Edition. Pp. 344. New York: Macmillan Company, 1917. Price, $1.40.

This book was written to fill a much-needed demand, to cover a brief but comprehensive course in organic chemistry for pre-medical or first year medical school students as well as for those requiring a short general knowledge of organic chemistry. It contains laboratory experiments which have been put in their proper places with the theoretical discussion so that the book may be used as a laboratory manual as well as a text book. The material has been presented in a novel way. It is divided into three parts. In the first part, the beginning deals with the explanation of the general principles underlying the determinations of purity, empirical and molecular formulas and structure. Then follows a careful study of the mode of preparation and chemical reactions of ethyl and methyl alcohol as well as a description of the chemical and physical properties and structure of the substances easily produced from them as ethyl ether, acetaldehyde and formaldehyde, acetic acid and formic acid, etc. The second part of the book is devoted to a systematic study of aliphatic compounds. The material in this part is almost identical with the corresponding chapters in the aliphatic section of the "Theoretical Organic Chemistry" by the same author. The order of presentation, however, is slightly changed and the chapters on nitroparaffins, sulfur compounds and metallic organic compounds have been omitted. No repetition is made of what occurs in the first part. The third part is a brief account of the more important compounds of the aromatic series presented in a very similar way to that in the "Theoretical Organic Chemistry" but considerably shortened.

In reviewing this little book, one finds in general, the same fault which characterizes most of the elementary books in organic chemistry, that the authors do not take the trouble to keep them strictly up to date in every respect. Thus, on page 38, one finds the statement "but the peroxide (referring to diethyl peroxide) has not yet been obtained though there is no apparent reason for its non-existence," although we find a thorough study of this compound in *Ber.*, **33**, 3388 (1900); again on page 159, one finds the old structural formula of cane sugar given although the evidence[1] is very strong that the older one is not correct; still again, in spite of the fact that the book was written primarily for medical school students, nearly a page is devoted to the estimation of urea by the hypobromite method when this has been shown to be inaccurate and has practically been displaced by the urease method.

In writing a text book of this type, one realizes the extreme difficulty

[1] *J. Chem. Soc.*, **109**, 1314 (1916).

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of the author to know what material should be included and what should be left out. It seems, however, unreasonable that even in a book of this size many pages should be devoted to a description of compounds of comparatively little practical or theoretical importance as, for example, two half pages to isocyanides, cyanuric acid and cyanates while not even a mention is made of one of the most important reagents in organic chemistry, the Grignard reagent.

Another point which can not be overlooked in reviewing this book is the too large proportion of space devoted to laboratory experiments, one hundred and seventy-seven in all. Many of these experiments are by no means easily carried out and are too difficult for the class of students for which the book is meant. Thus, one finds the preparation of phthalic acid from naphthalene, of salicylic acid from phenol, of benzaldehyde from benzyl chloride, of benzyl chloride from toluene, of phenyl hydrazine from aniline, of glycocoll from chloroacetic acid, of ethyl acetoacetate from ethyl acetate and many others, preparations in which much more advanced students often have serious trouble. To a teacher who has not had considerable experience in organic chemistry, the results that his class would obtain in these experiments might prove disconcerting.

In conclusion, it may be said that the material in this book is presented in a clear, concise and interesting way as in the other books by the same author and that any teacher of an elementary course in organic chemistry may well review it and consider carefully the mode of presentation of the subject. With some discrimination by those using it as a text and laboratory manual, this book should prove of value in the teaching of elementary organic chemistry.

ROGER ADAMS.

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with which has been incorporated the

American Chemical Journal

(Founded by Ira Remsen)

THE PERIODIC SYSTEM OF ELEMENTS.

BY CHARLES P. STEINMETZ.

Received January 18, 1918.

I.—The chemical and physical properties of the elements are functions of their atomic weights, in the periodic system of elements. The periodicity is all embracing and complete extending to practically all properties. However, if an attempt is made to represent this periodicity graphically, in tabular form, it is a failure. The usual form of representation is given in the table, Fig. 1, where however the last column again precedes the first column, that is, the representation should be on a cylinder, with Li following He, and Na following Ne, etc., or on a spiral.

The first period of 8 elements, from Li to Ne, is followed by the second period of 8 elements, from Na to A, which are close homologs of the first period. The third period starts with A, K and Ca, close homologs of the corresponding elements of the first 2 periods, but gradually the analogy becomes less in V, Cr, Mn, though there still are some analogies to the corresponding elements of the preceding periods: P, S, Cl. Then, in the triplet Fe, Co, Ni, the analogy with Ne and A entirely disappears. Then a partial analogy appears again in Cu, Zn, as sub groups of K, Ca, and finally, at the end of this period, in Se, Br, Kr, close homologs with S, Cl and A are again reached. We thus here have a double period of 18 elements. Then follows a second double period of 18 elements from Kr to I. Plotted in a table of 8 columns, Fig. 1, this double periodicity is not represented, and each column does not contain a series of homologs,

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	1	2	3	4	3/5	2/6	1/7	0/8-2	
x	Li.7	Be.9	B.11	C.12	N.14	O.16	H.1	He.4	0
x	Na.23	Mg.24	Al.27	Si.28	P.31	S.32	F.19	Ne.20	
x^2	K.39	Ca.40	Sc.44	× Ti.48	V.51	Cr.52	Cl.35.5	A.40	40
	Cu.63.5	Zn.65	Ga.70	Ge.72	As.75	Se.79	Mn.55	Fe.56 Co.59 Ni.59	
x^3	Rb.85	Sr.87	Yt.89	Zr.91	Nb.93	Mb.96	Br.80	Kr.83	80
	Ag.108	Cd.112	In.115	Sn.119	Sb.120	Te.127	—	Ru.102 Rh.103 Pd.107	
x^4	Cs.133	Ba.137	La.139	× Ce.140	Pr.141	Nd.144	I.127	Xe.130	120
	Eu.152	—	Gd.157	Tb.159	Dy.162	Ho.164	—	Sa.150	
	—	Yb.173	Lu.173	—	Ta.181	W.184	Er.168	Tm.169	160
	Au.197	Hg.201	Tl.204	Pb.207	Bi.208	—	—	Os.191 Ir.193 Pt.195	200
x^5	—	Ra.226	—	Th.232	— U 238			Nt.222	240

Fig. 1.

but 2 series, a main group: Li, Na, K, Rb, Cs, and a sub group: Cu, Ag, Au.

Plotting the periodic system in the form of Table I, shows the periodicity of the double periods, but does not show the periodicity between groups and sub groups, thus also gives an incomplete representation.

TABLE I.

..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	H
He	Li	Be	B	C	..	..	..	..	..	..	..	..	..	..	N	O	F
Ne	Na	Mg	Al	Si	..	..	..	..	..	..	..	..	..	..	P	S	Cl
A	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
Kr	Rb	Sr	Yt	Zr	Nb	Mb	..	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
Xe	Cs	Ba	La	Ce	Pr	Nd	..	Sa	..	..	Eu	..	Gd	Tb	Dy	Ho	Er
..	Tm	Yb	Lu	..	Ta	W	..	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	..	..
Nt	..	Ra	..	Th	..	U	..	..	..	..	..	..	..	..	..	..	..

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Going now beyond the 2 double periods, we come apparently to a quadruple period: starting with Cs and Ba as homologs to Rb and Sr, we then leave the analogy with the previous periods, in the rare elements from La to Lu, then return to homologs of the sub group, from Ta to Hg, and then to homologs of the main group, up to Nt. Then apparently follow some fragments of a second quadruple group.

Table I obviously would not represent the quadruple period.

The periodic system thus comprises 2 single periods, 2 double periods and a quadruple period with some fragments of a further period.

No way exists to represent graphically, by table, this multiple periodicity and thereby to show the periodic relation satisfactorily.

However, no reason exists, why this periodicity should be representable graphically on a plane, as in a table: if the properties of the elements are functions of their atomic weights, this function may be representable on a plane, or it may not. It is nothing uncommon that a mathematical function can not be represented in a plane. For instance, the distances of the cities on the earth are a function of their location, but this function can not be represented on a plane—but only on a sphere, because the earth is a sphere—and all geographical representations thus are necessarily distorted.

It is interesting to note for instance, that the double periods, from A to Kr, or from Kr to Xe, can be represented on a single sided ring, as shown in photographic representation in Figs. 2 and 3: as seen, this representation

Fig. 2.

Fig. 3.

shows both periodicities: Xe comes beneath Kr; Ag comes beneath Rb, but on the other side of the paper—and Cs again becomes beneath Rb, though on the other side of Ag, but coincident with it, thus showing the partial periodicity between sub group and main group, and at the same time the complete periodicity within the main groups, or within the sub groups.

It follows herefrom, that the periodicity function of the atomic weights can not be represented on a plane. The single sided ring, Figs. 2 and 3, only represents the double periods, but not the entire periodic system.

II.—However, when considering the representation of the function repre-

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senting the elementary properties by their atomic weight, in the periodic system, the natural procedure obviously is to consider the various functional representations devised in the theory of functions of mathematics, and it can be seen then, that the periodic system of elements, with its single, double and quadruple periodicities, can be completely represented by a Riemann surface with 2 singular points, at —40 and —130 approximately.

Let two planes A and B be related to each other so that the points $Z = x + jy$ of the plane A correspond to the points $W = u + jv$ of the plane B—where x and y, respectively, and u and v are the coördinates, and the points represented in the usual manner by a general number or complex quantity. Z for instance may represent the structure, W the atomic weight of the element.

Let now the relation between Z and W be given by an equation of the form

$$Z = \sqrt{W + 40} - 6.32. \qquad (1)$$

Suppose now, on the plane W, we start from a point W_0 and trace a line—over $W_1, W_2 \ldots$ back to W_0, in Fig. 4. Then the corresponding point Z moves from Z_0 over $Z_1, Z_2 \ldots$ back to Z_0. This however occurs only, if the path of W does not encircle the point $W = -40$.

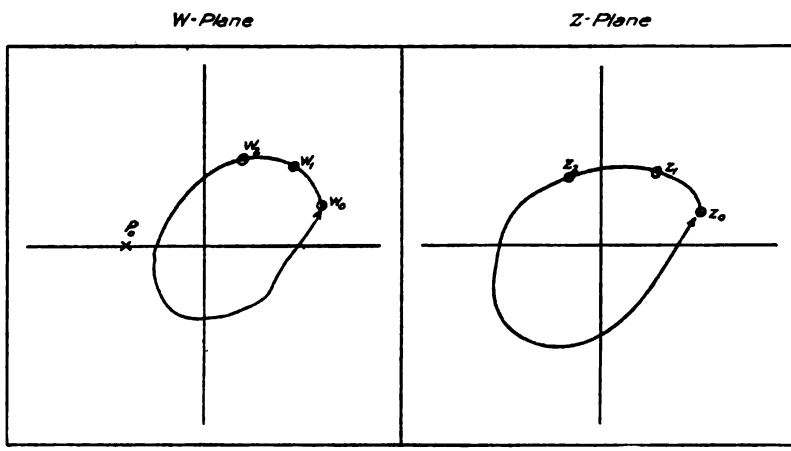

Fig. 4.

If however, in Fig. 5, the path of W encircles the singular point—P_0: $W = -40$, then, when completing the circuit from W_0 back to the same point, the path of Z does not close, but, beginning at Z_0, ends at Z_0', at a different point. Thus, functionally, the point W_0', to which we returned, although apparently coincident with W_0, is not the same point, as it corresponds to a different point Z_0'. Traversing once more a closed path, from W_0', corresponding to Z_0', then when returning to the starting point of W, we reach the starting point of Z_0, thus return to the starting

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point of W_0. Hence, if the path of W encloses the singular point —40, a double circuit of W corresponds to a circuit of Z. In other words, W is a double plane, and the two planes have one point $P_0 : W = -40$, in common, so that any closed path of W, which does not enclose $W = -40$,

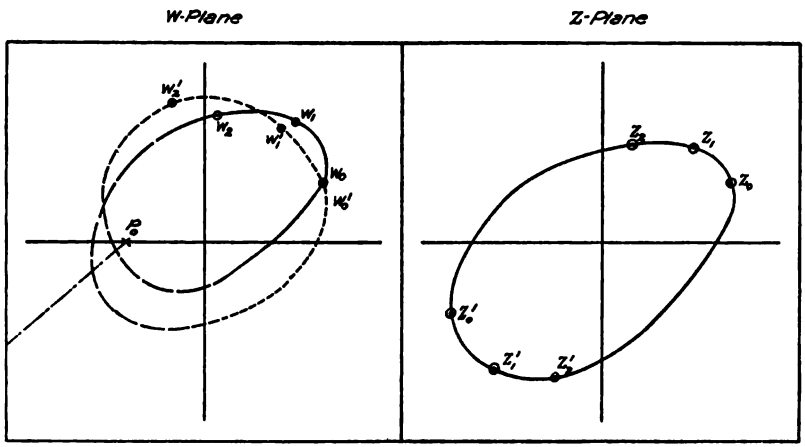

Fig. 5.

remains completely in one plane; a path of W, however, which encloses the singular point, does not close, but passes from the one plane to the other, and returns to the first plane and closes itself only after the second circuit, in other words gives a double periodicity.

Such a Riemann double plane with singular point at P_0, can be pictured as two planes fastened together at P_0, and intersecting each other, so that the lower plane passes into the upper, and the upper into the lower. This physically would require the two planes to intersect on a line from P_0 to ∞; the Riemann double plane however does not intersect, but only has the point P_0 in common, and thus is not physically representable, that is, the mathematical relations given above can not be represented in a physical plane, but nevertheless, show the functional relations quite real. Of the same nature apparently is the functional relation of the periodic system, and as such is represented by a Riemann plane.

Equation 1 represents only the single and the double periods, but not the quadruple periods, but to represent the latter, besides the singular point $P_0 = -40$, a second singular point of higher order would exist at $P_0' = -130$, thus giving a quadruple plane, with singular points at P_0 and P_0'. However, since the object of the discussion is merely to show the possibility of the complete representation of the periodic system by a Riemann plane, we do not need to enter further into the mathematics.

In Fig. 1 then are marked the singular points by crosses.

In Fig. 6 then is represented as illustration the first single period of the

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periodic system, from He to Ne. The Z plane shows the spiral giving the periodic relation, and the W plane the atomic weights as represented on the Riemann surface, in this case, on one plane of it.

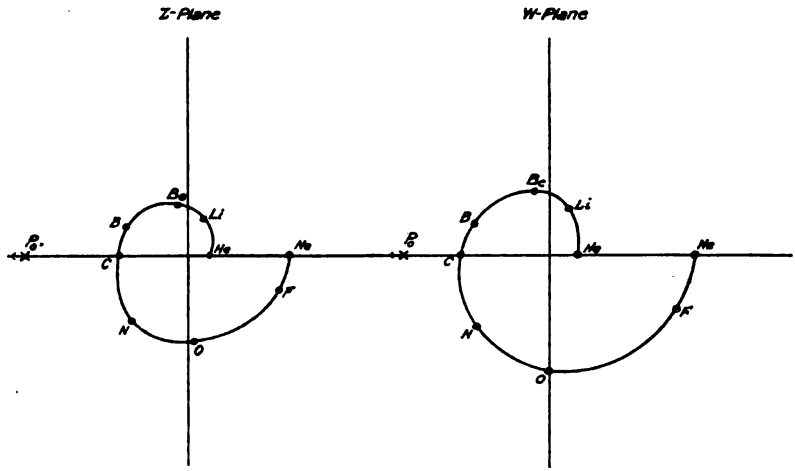

Fig. 6.

Fig. 7 shows the representation of the second double period, from Kr to Xe. The Z plane gives the single spiral functional relation, the W plane the corresponding representation of the atomic weights on the Riemann surface; starting from Kr and following the spiral over Rb, Sr, etc., when

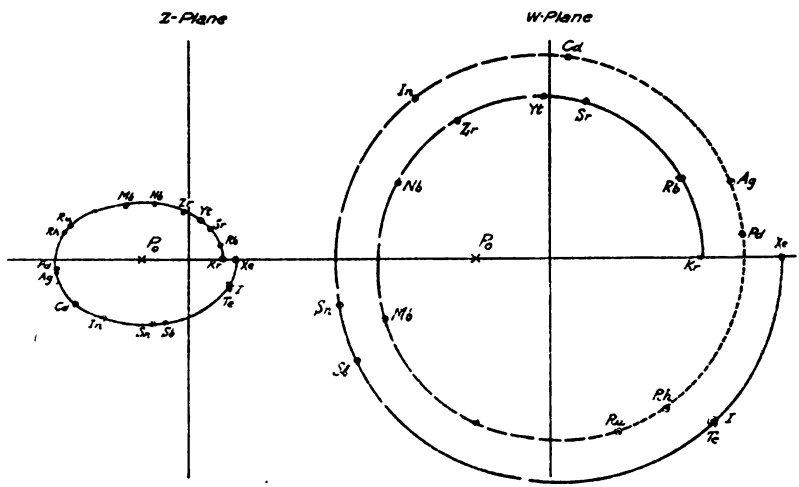

Fig. 7.

we come around again to Rh, Pd, Ag, we are in the other plane, and, following the spiral further, over Cd, In, etc., coming around once more, at Te, I, Xe we are again in the first plane.

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As further illustration is shown diagrammatically, in Fig. 8, the *W* or Riemann plane graphically representing the quadruple periodicity of the atomic weights from Xe to Nt, or the first quadruple period.

It follows herefrom:

The periodic system of elements, with its single, double and quadruple periodicities, can not be graphically illustrated on a plane, cylinder, etc., but it can be correctly represented on a Riemann surface with singular points at —40 and —130.

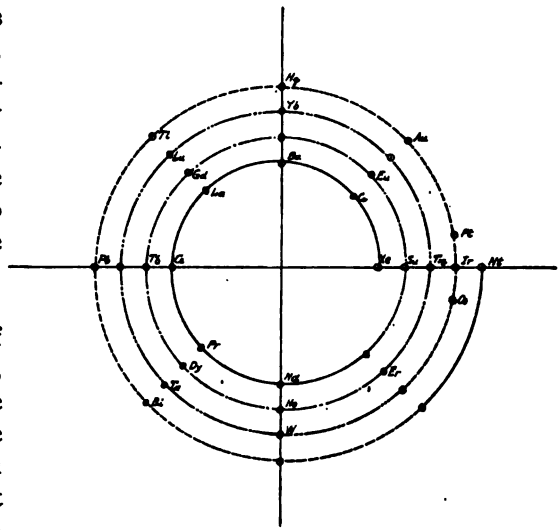

Fig. 8.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY. NO. 113.]

THE POTENTIALS OF THE BISMUTH-BISMUTHOXYCHLORIDE AND THE COPPER-CUPROUS-CHLORIDE ELECTRODES.

BY ARTHUR A. NOYES AND MING CHOW.

Received February 4, 1918.

CONTENTS.—1. Outline of the Investigation. 2. Electromotive-Force Measurements: General Description; Preparation of the Substances; Description of the Hydrogen-Bismuth Cells; The Experimental Data for the Hydrogen-Bismuth Cells; Description of the Hydrogen-Copper Cells; The Experimental Data for the Hydrogen-Copper Cells; The Experimental Data for the Bismuth-Copper Cells. 3. The Solubility of Cuprous Chloride in Hydrochloric Acid. 4. Calculation of the Specific Electrode Potentials: The Bismuthoxychloride Electrode; The Cuprous-Chloride Electrode; The Difference between the Two Specific Electrode Potentials. 5. The Heat Effects Attending the Cell Reactions. 6. The Equilibrium Measurements: Preliminary Experiments by F. H. Smyth; Apparatus and Materials; Experimental Method; The Experimental Data. 7. Calculation of the Equilibrium Constant at 75°. 8. Thermochemical Measurements of the Bismuth-Copper Reaction: Data Available; Plan of the New Determinations; The Apparatus and Materials; The Experimental Procedure; The Experimental Data. 9. The Heat Effect Attending the Bismuth-Copper Reaction. 10. The Equilibrium Constant at 25° and the Corresponding Difference in the Two Specific Electrode Potentials. 11. Summary.

1. Outline of the Investigation.

The purpose of this investigation was to determine the specific (or normal) potential of the electrode Bi + BiOCl, $\left\{\begin{matrix} H^+ \\ Cl^- \end{matrix}\right.$ and that of the

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electrode Cu + CuCl,Cl^-. The problem was attacked in two ways: first, by measuring the electromotive forces at temperatures between 0° and 50° of cells in which these two electrodes were combined with one another and of cells in which each of them separately was combined with a hydrogen electrode; and secondly, by determining the equilibrium conditions at 75° of the reaction[1]

$$3CuCl\ (s) + Bi\ (s) + H_2O = 2H^+Cl^- + BiOCl\ (s) + 3Cu\ (s).$$

Calorimetric measurements were also made of the heat effect attending this reaction, so as to enable its equilibrium constant to be calculated over to room temperature. These measurements consisted of two series, in which the bismuthoxychloride and the cuprous chloride were caused to react separately with metallic tin. From the equilibrium constant of this reaction the difference between the specific potentials of the two electrodes under investigation was calculated and compared with that derived from the electromotive-force measurements.

Data on cells containing bismuth electrodes have been published by various investigators. Of these the only ones capable of furnishing even an approximate value for the electrode potential of bismuth are those of Neumann[2] and Rothmund.[3] No data on the equilibrium between bismuth compounds and those of another metal are available.

We wish to express to Dr. J. H. Ellis our indebtedness for the great assistance he rendered us in connection with the thermochemical and electromotive-force measurements and in the preparation of the article for publication.

2. Electromotive-Force Measurements.

General Description.—The specific electrode potentials were determined by measuring the electromotive force at 15, 25, and 35° of the cells

$$H_2\ (\text{approx. 1 atm.}),\ HCl\ (0.001\text{–}0.5\ M)\ BiOCl\ (s) + Bi\ (s).$$

$$H_2\ (\text{approx. 1 atm.}),\ HCl\ (0.01\text{–}0.6\ M)\ CuCl\ (s) + Cu\ (s).$$

The apparatus used consisted of a hydrogen half-cell of the type used by Ellis[4] and of another half-cell containing four platinum spiral electrodes, each with a wire 6 cm. long and 0.06 cm. in diameter. These four electrodes were plated electrolytically either with bismuth or with copper; and the tubes containing them were filled with hydrochloric acid and a large quantity of solid bismuthoxychloride or of solid cuprous chloride mixed with finely divided copper. The hydrogen side of the cell was charged with pure hydrochloric acid of the same concentration containing

[1] The letter (s) appended to a symbol shows that the substance is present in the solid state, (g) that it is in the gaseous state.

[2] *Z. phys. Chem.*, 14, 193–230 (1894).

[3] *Ibid.*, 15, 18 (1894).

[4] THIS JOURNAL, 38, 741 (1916).

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no bismuth or copper; hydrogen was furnished to it by an electrolytic hydrogen generator.

Preparation of the Substances.—The best commercial hydrochloric acid was used. The cuprous chloride employed was a sample from Kahlbaum.

Metallic copper was prepared by shaking for several days copper sulfate solution with a quantity of zinc insufficient to precipitate all the copper; it was washed with dilute copper sulfate solution to remove all the zinc, then with water and with dilute hydrochloric acid.

Metallic bismuth was prepared by depositing it on a platinum cathode by electrolyzing with high current density a 2 *M* hydrochloric acid solution in contact with solid bismuthoxychloride, using a copper anode in a separate vessel connected with the cathode compartment by a siphon tube.

Bismuthoxychloride was prepared from Kahlbaum's bismuth nitrate by treating it with strong hydrochloric acid and evaporating off most of the acid. The bismuthoxychloride was then dissolved in strong hydrochloric acid and reprecipitated by pouring into a large volume of water, after which it was washed by decantation, redissolved in hydrochloric acid, and reprecipitated by pouring the hydrochloric acid solution, with vigorous stirring, into a quantity of water insufficient to precipitate all the bismuth.

These substances were all preserved under dilute hydrochloric acid, and were washed just before use with hydrochloric acid of the concentration to be used in the experiment.

Description of the Hydrogen-Bismuth Cells.—To produce the coating of bismuth on the four platinum spirals, the part of the cell containing these spirals was filled with a 5 *M* hydrochloric acid solution nearly saturated with bismuthoxychloride, 3 auxiliary platinum anodes were inserted in such positions as to produce the most uniform deposit of bismuth all over the spirals, and electrolysis was conducted for about 6 hours with a current density varying from about 0.1 ampere per sq. cm. at the beginning to about 0.4 ampere per sq. cm. at the end. The deposit of bismuth obtained in this manner was dark gray and spongy; its inner parts adhered well to the platinum spiral, but the outer layers were less coherent. The exact manner of preparing the bismuth coating was found not to be essential; thus 3 sets of 4 electrodes made up without following closely the above procedure were found to give mutually consistent results.

After the electrolysis was finished, the electrodes were washed 10 or more times with 0.2 *M* hydrochloric acid, allowing them to stand in contact with the acid for half an hour each time. They were then washed 4 or 5 times in the same manner with acid of the concentration to be used in the first set of experiments. A mixture of solid bismuthoxychloride and finely divided metallic bismuth was also washed 5 to 8 times with acid of this concentration, and then a suspension of this mixture in the acid was intro-

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duced into the side of the cell containing the bismuth electrodes so as to fill it completely. The hydrogen side of the cell was partially filled with pure acid of the same concentration, but containing no bismuth. Liquid connection between the hydrogen and bismuth half-cells was made by sucking over a small amount of hydrochloric acid from the hydrogen half-cell so as to fill the connecting tube. All the ground joints of the cell were sealed air-tight with beeswax, to prevent evaporation of the solution or entrance of oxygen.

The cell was then set up in the thermostat at 25° and hydrogen was passed through the hydrogen half-cell. After about 3 hours the electromotive force of the hydrogen half-cell against each of the 4 bismuth electrodes was measured by means of a Leeds and Northrup potentiometer reading to 0.01 millivolt. The 4 values thus obtained usually agreed within about 0.0002 volt. The cell was then shaken at intervals of a few hours so as to ensure saturation of the hydrochloric acid with the bismuth-oxychloride at 25°. After a day of this treatment the bismuth electrodes usually agreed within 0.0001 volt. Readings of electromotive force, cell temperature, and the atmospheric pressure were made at intervals until the electromotive force showed constancy within 0.00005 volt over a period of 5 to 10 hours. The cell temperature was then changed to 15° or 35°, and this procedure was repeated. The response to temperature changes was rapid, and no temperature hysteresis was noted.

After measurements of the electromotive force of the cell at each desired temperature had been obtained, the cell was washed and filled with hydrochloric acid of a new concentration and the same procedure was repeated.

The Experimental Data for the Hydrogen-Bismuth Cells.—Table I contains the original data for the bismuth cells at each temperature and concentration studied. The electromotive-force values are those taken after the cell had assumed a constant electromotive force. The first column

TABLE I.—ELECTROMOTIVE FORCES OF THE HYDROGEN-BISMUTH CELLS.

Mols HCl per 1000 g. H_2O.	Cell temp.	Hydrogen pressure.	Observed electromotive forces.				Corrected E. M. F.
			Cell I.	Cell II.	Cell III.	Cell IV.	
0.000983	25.00	73.79	0.28208	0.28211	0.28216	0.28209	0.28249
0.001010	25.00	74.05	0.28182	0.28178	0.28181	0.28186	0.28212
0.003175	25.00	74.19	0.26041	0.26045	0.26046	0.26042	0.26071
0.009022	25.00	74.20	0.24256	0.24263	0.24267	0.24262	0.24293
0.02007	25.00	74.17	0.22912	0.22915	0.22917	0.22916	0.22947
0.04586	25.00	74.18	0.21575	0.21580	0.21577	0.21573	0.21606
0.1041	15.00	74.11	0.20407	0.20409	0.20414	0.20417	0.20447
0.1041	25.00	73.61	0.20175	0.20175	0.20179	0.20174	0.20221
0.1041	35.00	71.76	0.19937	0.19938	0.19936	0.19934	0.20011
0.2304	15.00	73.28	0.19115	0.19113	0.19120	0.19114	0.19160
0.2304	25.00	72.46	0.18825	0.18825	0.18830	0.18822	0.18887
0.2304	35.00	69.49	0.18500	0.18497	0.18499	0.18500	0.18617
0.5005	25.00	75.22	0.17547	0.17546	0.17556	0.17552	0.17563

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of the table contains the concentration of hydrochloric acid expressed in mols of HCl per 1000 g. water, the second the temperature of the cell, and the third the corrected hydrogen pressure in centimeters of mercury at the hydrogen electrode, obtained by applying to the barometric reading the corrections described by Ellis.[1] The next 4 columns contain the observed electromotive forces of the hydrogen electrode against each of the 4 bismuth electrodes. The last column contains the means of these values corrected to a hydrogen pressure of exactly one atmosphere with the aid of the ordinary logarithmic formula.

Description of the Hydrogen-Copper Cells.—The copper electrodes were prepared by electroplating the spiral platinum wires of the cell with copper from a 0.5 *M* copper sulfate solution, using the same current densities as for the bismuth plating. The coating obtained was a bright red, spongy mass. The electrodes were washed in the same manner as were the bismuth electrodes. Three sets of 4 copper electrodes were made up in this manner, and gave mutually consistent results.

The filling of the cell with hydrochloric acid, cuprous chloride, and finely divided metallic copper was performed in the same manner as the analogous operations for the bismuth cell; but care was taken to make the operation as rapid as possible, so as to avoid any oxidation of the cuprous chloride. The cell was never exposed to strong light, so as to prevent darkening of the cuprous chloride; but no change in electromotive force was noticed in the cases when the cuprous chloride was allowed to darken.

The four cuprous-chloride electrodes showed agreement within 0.0003 volt 3 or 4 hours after setting up the apparatus in the thermostat, but the electromotive force of the whole cell always dropped slowly throughout the course of a day. It then became more constant, and the separate electrodes showed better agreement, usually within 0.0001 volt. Shaking the cell then caused the electromotive force to rise to a value somewhat lower than the original value, but after standing the electromotive force dropped again. Successive shakings caused smaller and smaller rises of electromotive force, until finally no further change was caused either by shaking the cell or by letting it stand. This phenomenon is to be explained by the supposition that the cell as first set up contained a small amount of cupric ion; that this cupric ion was reduced to cuprous ion in the neighborhood of the copper electrode; that by the shaking new amounts of cupric ion were brought up to the copper electrode and slowly reduced, until finally cupric ion was present at the equilibrium concentration and the electromotive force no longer changed on shaking or standing. It was found that the presence of a large amount of finely divided electrolytic copper in the cell greatly reduced the time necessary to secure a constant value of the electromotive force.

[1] *Loc. cit.*

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The Experimental Data for the Hydrogen-Copper Cells.—Table II contains the observed electromotive forces of the hydrogen electrode against each of the 4 copper electrodes at each concentration and temperature. The last column contains the mean value of the electromotive force of the hydrogen-copper cell at each temperature and concentration, after correction has been applied to refer the value to a hydrogen pressure of exactly one atmosphere.

TABLE II.—THE ELECTROMOTIVE FORCES OF THE HYDROGEN-COPPER CELLS.

Mols HCl per 1000 g. H_2O.	Cell temp.	Hydrogen pressure.	Observed electromotive forces. Cell I.	Cell II.	Cell III.	Cell IV.	Corrected E. M. F.
0.01447	25.00	74.03	0.34681	0.34694	0.34659	0.34675	0.34718
0.01447	35.00	72.06	0.34677	0.34677	0.34645	0.34655	0.34643
0.04304	25.00	73.29	0.29188	0.29191	0.29172	0.29173	0.29227
0.09596	15.00	75.50	0.25314	0.25330	0.25334	0.25332	0.25340
0.09596	25.00	74.10	0.25131	0.25172	0.25170	0.25175	0.25204
0.09596	35.00	72.42	0.24983	0.24992	0.24994	0.24974	0.25049
0.1876	15.00	75.03	0.22126	0.22115	0.22114	0.22118	0.22134
0.1876	25.00	74.22	0.21895	0.21884	0.21885	0.21886	0.21911
0.1876	35.00	72.74	0.21611	0.21606	0.21601	0.21600	0.21663
0.3253	25.00	73.48	0.19115	0.19116	0.19115	0.19115	0.19158
0.3253	35.00	71.34	0.18743	0.18744	0.18740	0.18740	0.18823
0.6310	25.00	73.33	0.15741	0.15756	0.15750	0.15760	0.15798

The Experimental Data for the Bismuth-Copper Cells.—Owing to the fact that the heat effect calculated from the foregoing electromotive forces at the different temperatures did not agree well with the result obtained from the thermochemical measurements described in Section 8 of this article, an independent series of electromotive-force measurements was undertaken several months after those already described were completed, in order to check the accuracy of the latter. These measurements were made with the cells

Bi (s) + BiOCl (s), HCl(0.0627 and 0.0966 *M*), CuCl (s) + Cu (s).

The bismuth electrodes and the copper electrodes were prepared as for the previous measurements. Each half-cell contained 2 electrodes of the same kind. By the 4 combinations of these electrodes 4 observed values of the electromotive force were obtained. These are recorded in Table III. The last column contains the mean of the 4 observed values.

TABLE III.—ELECTROMOTIVE FORCES OF THE BISMUTH-COPPER CELLS.

Mols HCl per 1000 g. H_2O.	Cell temp.	Observed electromotive forces. Cell I.	Cell II.	Cell III.	Cell IV.	Average E. M. F.
0.06270	15.00°	0.06104	0.06100	0.06103	0.06102	0.06102
0.06270	25.00°	0.06212	0.06214	0.06212	0.06210	0.06212
0.06270	35.00°	0.06327	0.06323	0.06327	0.06324	0.06325
0.09661	0.00°	0.04552	0.04571	0.04570	0.04550	0.04561
0.09661	25.00°	0.04842	0.04838	0.04845	0.04836	0.04840
0.09661	50.00°	0.05008	0.05025	0.05023	0.05009	0.05016

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3. The Solubility of Cuprous Chloride in Hydrochloric Acid.

For an exact interpretation of the electromotive-force results it is necessary to know the solubility of cuprous chloride in hydrochloric acid at different concentrations and the nature of the complex ions that result. The investigations of Bodländer and Storbeck[1] have shown that cuprous chloride is present in chloride solutions substantially only in the form of the complex anion $CuCl_2^-$ so long as the chloride solution is of moderate concentration, namely from about 0.05 to 0.30 N. In more dilute solutions a considerable proportion of cupric chloride $CuCl_2$ is present, and in much more concentrated ones a large proportion of the more complex cuprous anion $CuCl_3^=$ exists.

The equilibrium constant K of the reaction $CuCl\ (s) + Cl^- = CuCl_2^-$, given by the expression $(CuCl_2^-)/(Cl^-) = K$, may be found from solubility determinations in moderately concentrated chloride solutions, by taking the ratio of the total dissolved copper (ΣCu) to the difference ($\Sigma Cl - 2\Sigma Cu$) between the total chloride and twice the total copper concentration, it being assumed hereby that the complex compound $H^+CuCl_2^-$ has the same ionization as hydrochloric acid.

Determinations of the solubility of cuprous chloride in dilute hydrochloric acid solutions at 15° have been made by Abel;[2] but his results show such irregularities and sudden changes in the values of the calculated constants that they can be regarded as only roughly approximate. The best existing determinations of the equilibrium constant in question seem to be those of Bodländer and Storbeck, who found at 16° for this constant the values 0.04934 and 0.04963 (mean 0.0495) by determining the solubility of cuprous chloride in potassium chloride solutions which were 0.1 and 0.2 N, respectively.[3]

As values were needed at higher temperatures, new determinations of the solubility of cuprous chloride in hydrochloric acid solutions at 25° were carried out in the course of the present work. Precipitated cuprous chloride and precipitated copper were shaken at 25° for 10 days with hydrochloric acid solutions of various concentrations, namely, 1.1650, 0.3165, 0.2156, and 0.0978 M. The total chloride concentration of the resulting solutions was found by precipitation as silver chloride and the total dissolved copper by electrolysis, after evaporation with nitric acid. Table IV gives the results obtained. The first column gives the total chloride concentration (ΣCl); the second column gives the total concentration of dissolved copper (ΣCu) and the third column shows the value of the con-

[1] *Z. anorg. Chem.*, **31**, 1, 458 (1902).

[2] *Ibid.*, **26**, 361 (1901).

[3] Abel's constants at 15° for HCl concentrations between 0.093 and 0.53 M vary irregularly between 0.052 and 0.068. See Abegg's *Handbuch anorg. Chem.*, **1**, II, 507 (1908).

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stant K equal to $\Sigma Cu/(\Sigma Cl - 2\Sigma Cu)$. All concentrations are expre in mols per 1000 g. of water.

TABLE IV.—SOLUBILITY OF CUPROUS CHLORIDE IN HYDROCHLORIC ACID AT

ΣCl.	ΣCu.	K.
1.2815	0.1165	0.1111
0.3364	0.01988	0.0671
0.2290	0.01340	0.0662
0.1038	0.00596	0.0650

In view of these results we may adopt as the best value of the cons at 25° the mean of the last three values, namely 0.0661.

A value of this constant at 75° can be derived from the equilibrium ı surements recorded below in Table IX. Namely, by subtracting fron chlorine concentration (0.4083) twice the copper concentration (2 × 0.0 and 5 times the bismuth concentration (5 × 0.00206), we get the con tration of the uncombined chloride (0.2446) and by dividing the co concentration by this value we get for the constant K at 75° the v 0.314.

Out of these 2 values of the constant (at 75° and 25°) the value of ∠ the heat absorbed by the solution of 1 mol of CuCl in dilute hydroch acid, was calculated by means of the van't Hoff equation.

$$\log_{10} \frac{K_2}{K_1} = \frac{\Delta H_S}{2.303R} \frac{T_2 - T_1}{T_1 T_2}.$$

The value of ΔH_S was thus found to be 6440 cal.

With the aid of this value the solubility constants $(CuCl_2^-)/(Cl^-$ 0°, 15°, 35°, and 50° were calculated by the same equation. The fol ing values[1] were thereby obtained:

0.0244 at 0°; 0.0453 at 15°; 0.0661 at 25°; 0.0940 at 35°; 0.153 at ;

4. Calculation of the Specific Electrode Potentials from the Ele motive Forces.

The Bismuthoxychloride Electrode.—The specific potential of the muthoxychloride electrode may be calculated from the corrected ele motive forces E of the hydrogen-bismuth cells given in Table I, by m of the following formula, in which c represents the concentrations a the activity coefficients of the hydrochloric acid in the cells:

$$E_{BiOCl} = -E - \frac{RT}{3F} \log (c\alpha)^2$$

For in the cell

$$H_2 \text{ (1 atm.)}, \left\{\begin{matrix} H^+ \text{ at } c\alpha\, M \\ Cl^- \text{ at } c\alpha\, M \end{matrix}\right\}, \left\{\begin{matrix} BiOCl \text{ (s)} \\ Bi \text{ (s)} \end{matrix}\right\}, \left\{\begin{matrix} H^+ \text{ at } 1\, M \\ Cl^- \text{ at } 1\, M \end{matrix}\right\}, H_2 \text{ (1 a}$$

[1] The value at 16° is calculated to be 0.0473 which is in good agreement wit value (0.0495) found by Bodländer and Storbeck.

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whole electromotive force is $E + \bar{E}_{BiOCl}$; the change in state which takes place when 3 faradays pass through is

$$H^+ \text{ (at 1 } M) + Cl^- \text{ (at 1 } M) = H^+ \text{ (at } c\alpha\ M) + Cl^- \text{ (at } c\alpha\ M).$$

The first column of Table V gives the temperature, and the second the values of the hydrochloric acid concentration (c). The third column shows the values of the activity coefficient (α) of hydrochloric acid as determined by Noyes and Ellis.[1] The fourth column gives the values taken from Table I of the corrected electromotive force of the corresponding bismuth cell. And the last column gives the values of the specific potential of the bismuth-oxychloride electrode calculated by the above formula.

TABLE V.—THE SPECIFIC POTENTIAL OF THE BISMUTHOXYCHLORIDE ELECTRODE.

Temperature	Mols HCl per 1000 g. water.	Activity coefficient.	Corrected cell E. M. F.	Specific potential.
25.00°.....	0.5003	0.760	0.17563	—0.1591
	0.2304	0.788	0.18887	—0.1597
	0.1041	0.820	0.20221	—0.1601
	0.04586	0.859	0.21606	—0.1607
	0.02007	0.898	0.22947	—0.1607
	0.00902	0.937	0.24293	—0.1612
	0.00318	0.978	0.26071	—0.1618
	0.00101	0.990	0.28212	—0.1638
	0.000984	0.991	0.28249	—0.1637
			Best value,	—0.1599
15.00°.....	0.2304	0.791	0.19160	—0.1633
	0.1041	0.822	0.20447	—0.1638
			Mean,	—0.1635
35.00°.....	0.2304	0.784	0.18617	—0.1561
	0.1041	0.816	0.20011	—0.1565
			Mean,	—0.1563

The first value of the specific potential at 25° is not accurate because no account has been taken of the appreciable quantity of bismuth which dissolves in hydrochloric acid at this concentration. The last 2 values may also be inexact because of experimental error at the very low concentrations. The intermediate values, though they do not seem to be subject to experimental error, yet show a progressive change, amounting to about 2 millivolts between 0.23 and 0.003 M. As best value we have adopted —0.1599, which is the mean value for the two concentrations 0.2304 and 0.1041 molal, for the reason that it is then directly comparable with the mean values at 15° and 35°.

The Cuprous-Chloride Electrode.—The specific potential $\bar{E}_{CuCl}$ of the copper–cuprous = chloride electrode can be calculated from the corrected electromotive force E of the hydrogen-copper cells given in Table II by

[1] THIS JOURNAL, 39, 2543 (1917).

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the following formula, in which (Cl^-) represents the chloride-ion concentration in the copper half-cell, (H^+) the hydrogen-ion concentration in the hydrogen half-cell, c the concentration of the acid, α its activity coefficient, and K the solubility constant of cuprous chloride derived in the preceding section:

$$\dot{E}_{CuCl} = -E - \frac{RT}{F} \log (H^+)(Cl^-) = -E - \frac{RT}{F} \log \frac{(c\alpha)^2}{(1 + K)}$$

In the last member of this equation the chloride-ion concentration is replaced by a quantity obtained by correcting the concentration of the hydrochloric acid in the cell for that of the cuprous chloride dissolved in the form of the complex $H^+CuCl_2^-$ with the help of the solubility constant K, and multiplying the result by the activity coefficient at that concentration. The concentrations of the dissolved cuprous chloride are given in the third column of the table. The assumption is made in these calculations that the complex acid is ionized to the same degree as hydrochloric acid, and that the mobility of the ion $CuCl_2^-$ is the same as that of the Cl^- ion, so that the liquid potential of the cell is negligibly small.

We have also calculated another specific potential defined so as to represent the potential when the total anion concentration $(Cl^- + CuCl_2^-)$ is 1 M. The computation was made by the following equation:

$$\dot{E}_{CuCl} = -E - \frac{RT}{F} \log (c\alpha)^2$$

The specific potentials calculated on these two bases are given in the columns headed I and II, respectively.

TABLE VI.—THE SPECIFIC POTENTIAL OF THE CUPROUS CHLORIDE ELECTRODE.

Temperature.	Mols HCl per 1000 g. water.	Mols CuCl per 1000 g. water.	Activity coefficient.	Corrected E. M. F.	Specific potential. I.	Specific potential. II.
25.00°.....	0.6310	0.0391	0.758	0.15798	—0.1185	—0.1201
	0.3253	0.0204	0.776	0.19158	—0.1191	—0.1209
	0.1876	0.0116	0.797	0.21911	—0.1199	—0.1215
	0.09596	0.0060	0.825	0.25204	—0.1201	—0.1218
	0.04304	0.0027	0.855	0.29227	—0.1210	—0.1226
	0.01447	0.0009	0.913	0.34718	—0.1233	—0.1249
				Best value,	—0.1200	—0.1216
15.00°.....	0.1876	0.00820	0.800	0.22134	—0.1261	—0.1271
	0.09596	0.00417	0.827	0.25340	—0.1265	—0.1276
				Best value,	—0.1263	—0.1274
35.00°.....	0.3253	0.0279	0.772	0.18823	—0.1125	—0.1149
	0.1876	0.0161	0.796	0.21663	—0.1133	—0.1157
	0.09596	0.00824	0.821	0.25049	—0.1132	—0.1156
				Best value,	—0.1132	—0.1156

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The "best values" have been derived by taking the means of the values at 0.1876 and 0.09596 *M*; for at the larger and smaller acid concentrations there are present considerable quantities of the bivalent cuprous anion $CuCl_3^-$ and of cupric chloride, respectively.

The Difference between the Two Specific Electrode Potentials.—The difference between the specific potential of the bismuthoxychloride electrode and that of the cuprous chloride electrode (computed for the case the chloride ion is 1 *M*) can be calculated from the average values of the electromotive force E of the bismuth-copper cells given in Table III, by the following equation, in which $(Cl^-)_C$ and $(Cl^-)_B$ represent the chloride-ion concentration in the copper half-cell and in the bismuth half-cell respectively, (H^+) the hydrogen-ion concentration in each half-cell, *c* the concentration of the acid in the cell, α its activity coefficient, and *K* the solubility constant of cuprous chloride defined as in Section 3 above.

$$\bar{E}_{BiOCl} - \bar{E}_{CuCl} = E + \frac{RT}{3F} \log \frac{(H^+)^2(Cl^-)^3_C}{(Cl^-)_B} = E + \frac{RT}{3F} \log \frac{(c\alpha)^4}{(1 + K)^2}.$$

The difference between the 2 specific potentials has also been calculated for the case where the cuprous chloride potential is understood to refer to a total anion concentration $(Cl^- + CuCl_2^-)$ of 1 *M*. These calculations were made by an equation differing from that given above only by omission of the factor $(1 + K)^2$.

These specific potential differences are given in Table VII; the first type in the column headed I, and the second type in that headed II.

TABLE VII.—DIFFERENCES BETWEEN THE SPECIFIC POTENTIALS OF THE BISMUTHOXYCHLORIDE AND THE CUPROUS CHLORIDE ELECTRODES.

Temperature.	Mols HCl per 1000 g. water.	Activity coefficient.	Average E. M. F.	Specific potential difference. I.	Specific potential difference. II.
15.00°	0.06270	0.841	0.06102	—0.03745	—0.03636
25.00°	0.06270	0.845	0.06212	—0.04013	—0.03850
35.00°	0.06270	0.847	0.06325	—0.04302	—0.04063
0.00°	0.09661	0.827	0.04561	—0.03426	—0.03369
15.00°	0.09661	0.823	(0.04757)	(—0.03772)	(—0.03650)
25.00°	0.09661	0.821	0.04840	—0.04002	—0.03838
35.00°	0.09661	0.818	(0.04923)	(—0.04330)	(—0.04073)
50.00°	0.09661	0.814	0.05016	—0.04821	—0.04425

The following summary shows how well these directly determined differences agree with those found by subtracting from one another the separate potentials derived from the measurements with the hydrogen cells and given in Tables V and VI. The following values correspond to those for the cuprous chloride half-cell with the chloride-ion concentration 1 *M* (those given under I in the tables). The values given in the last row are the averages derived from the two series of measurements in Table VII, values at 15 and 35° being obtained for the second of these series by interpolation.

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TABLE VIII.—SUMMARY OF THE AVERAGE VALUES OF THE SPECIFIC ELECTRODE POTENTIALS.

Electrode.	15.00°.	25.00°.	35.00°
Bismuthoxychloride	—0.1635	—0.1599	—0.1563
Cuprous chloride	—0.1263	—0.1200	—0.1132
Difference (by subtraction)	—0.0372	—0.0399	—0.0431
Difference (directly deter.)	—0.0376	—0.0401	—0.0432

5. The Heat Effects Attending the Cell Reactions.

From the specific electrode potentials ($\bar{E}_1$ and $\bar{E}_2$) at 15 and 35° given in the preceding paragraph the increase in heat-content ΔH attending the reaction taking place in each of the two cells when N faradays pass through it can be calculated by the Gibbs-Helmholtz equation, best written in the following form:

$$\int_{T_1}^{T_2} \Delta H \frac{dT}{T^2} = \mathrm{N_F} \left(\frac{\bar{E}_2}{T_2} - \frac{\bar{E}_1}{T_1} \right)$$

In the case of the bismuth cell ΔH may be considered constant, and the integral is equal to $\Delta H\ (T_2 - T_1)/T_1T_2$. To calculate the heat content increase, ΔH_A, which attends the change in state (A):

(A) $\mathrm{Bi\,(s) + H^+Cl^-\ (in\ \infty\ Aq) + H_2O = BiOCl\,(s) + 3/2H_2\ (1\ atm.)}$,

we have therefore the numerical expression

$$\Delta H_A \frac{20.0}{288.1 \times 308.1} = \frac{3 \times 96500}{4.182} \left(\frac{-0.1563}{308.1} - \frac{-0.1635}{288.1} \right).$$

The copper cell corresponding to the specific potentials given under II in Table VI may be formulated as follows:

$$\mathrm{Cu(s) + CuCl\,(s)}, \left\{ \frac{\mathrm{Cl^-}\ (1/(1+K))\ M}{\mathrm{CuCl_2^-}\ (K/(1+K))\ M} \right\} \Bigg\| \mathrm{H^+}\ (1\ M),\ \mathrm{H_2}\ 1\ (\mathrm{atm.}).$$

The heat content increase in this cell is that attending the two changes in state expressed by the following equations, in which K represents the solubility constant $(\mathrm{CuCl_2^-})/(\mathrm{Cl^-})$ considered in Section 3, and $\mathrm{T_H}$ the transference number of the hydrogen ion in dilute hydrochloric acid solution.

(B) $\mathrm{Cu\,(s) + H^+Cl^-\ (in\ \infty\ Aq) = CuCl\,(s) + {}^1/_2H_2\ (1\ atm.)}$.

(C) $\mathrm{T_H} \dfrac{K}{1+K}\ \mathrm{CuCl_2^-\ (in\ \infty\ Aq)} =$

$$\mathrm{T_H} \frac{K}{1+K}\ \mathrm{CuCl\ (s)} + \mathrm{T_H} \frac{K}{1+K}\ \mathrm{Cl^-\ (in\ \infty\ Aq)}.$$

The factor $\mathrm{T_H}$ arises from the consideration that of the 1 mol of $\mathrm{H^+Cl^-}$ destroyed by reaction B only the fraction $\mathrm{T_H}$ disappears at the copper electrode, in consequence of the transference in the cell. The heat content increase ΔH is therefore the sum of two heat contents which may be expressed by the following equation, in which ΔH_B and ΔH_C are the heat

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content increases attending changes in state (B) and (C), and ΔH_S is, as in Section 3, that attending the change in state: CuCl (s) + Cl^- (in ∞ Aq) = $CuCl_2^-$ (in ∞ Aq).

$$\Delta H = \Delta H_B + \Delta H_C = \Delta H_B - T_H \frac{K}{1 + K} \Delta H_S.$$

In the integration ΔH_B and ΔH_S may be regarded as constant; but $T_H K/(1 + K)$ changes rapidly with the temperature, and must be expressed as a function of it. The following function reproduces the results sufficiently well.[1]

$$T_H \frac{K}{1 + K} = -0.0099 + 9.76 \times 10^{-22} T^8.$$

Introducing this function and the value 6440 for ΔH_S derived in Section 3, and for $\bar{E}_2$ and $\bar{E}_1$ the values at 35 and 15° given in the last column of Table VI, we get the following numerical expression for ΔH_B, the heat content increase attending change in state (B) at 25°:

$$\left(\Delta H_B + (0.0099 \times 6440)\right)\left(\frac{20.0}{308.1 \times 288.1}\right) - \left(6440 \times 9.76 \times 10^{-22} \times \frac{1}{7}(308.1^7 - 288.1^7)\right) = \frac{96500}{4.182}\left(\frac{-0.1156}{308.1} - \frac{-0.1274}{288.1}\right)$$

The increases of the heat content so calculated are +18,500 cal. for the bismuth reaction (A), and +7190 cal. for the copper reaction (B). We may, therefore, write the following thermochemical equations applicable at 25°:

$$Bi\,(s) + H^+Cl^-\,(\text{in } \infty \text{ Aq}) + H_2O = BiOCl\,(s) + 3/2H_2\,(1 \text{ atm.}) \quad -18{,}500 \text{ cal.}$$

$$Cu\,(s) + H^+Cl^-\,(\text{in } \infty \text{ Aq}) = CuCl\,(s) + \tfrac{1}{2}H_2\,(1 \text{ atm.}) \quad -7190 \text{ cal.}$$

Multiplying the second of these equations by 3 and subtracting it from the first equation, we get the following provisional equation:

$$Bi\,(s) + 3CuCl\,(s) + H_2O = 3Cu\,(s) + BiOCl\,(s) + 2H^+Cl^-\,(\text{in } \infty \text{ Aq}) + 3070 \text{ cal.}$$

[1] The data from which this function is derived and the degree of its correspondence with them are shown in the following table. The values of T_H are computed from the ion conductances given by Johnston (THIS JOURNAL, 31, 1015 (1909)). Those of $K/(1 + K)$ are computed from the values of the solubility constant K given in Section 3. The product of these two quantities is shown in the next to last row of the table; and the value of the same quantity calculated by the above-given empirical temperature function is shown in the last row.

t	0°	15°	25°	35°	50°
T_H	0.854	0.832	0.823	0.813	0.800
$K/(1 + K)$	0.0238	0.0433	0.0620	0.0859	0.1326
$T_H K/(1 + K)$ (obs.)	0.0203	0.0360	0.0510	0.0698	0.1061
$T_H K/(1 + K)$ (calc.)	0.0203	0.0364	0.0510	0.0694	0.1061

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Independent values for this last heat-quantity can be obtained from the specific potentials derived from the measurements with the bismuth-copper cells and recorded in the last column of Table VII. The heat content increase attending the passage of three faradays through these cells is that corresponding to the changes in state expressed by the two equations

$$(D)\ \mathrm{Bi\,(s)} + 3\mathrm{CuCl\,(s)} + \mathrm{H_2O} = 3\mathrm{Cu\,(s)} + \mathrm{BiOCl\,(s)} + 2\mathrm{H^+Cl^-(in\,\infty\,Aq)}.$$

$$(E)\ \frac{3T_H K}{1+K}\,\mathrm{CuCl\,(s)} + \frac{3T_H K}{1+K}\,\mathrm{Cl^-\,(in\,\infty\,Aq)} = \frac{3T_H K}{1+K}\,\mathrm{CuCl_2^-\,(in\,\infty\,Aq)}.$$

The factor $3T_H$ in the last equation arises from the consideration that $3Cl^-$ are produced by the electrode process at the copper electrode and that $3(1 - T_H)Cl^-$ are transferred from that electrode to the bismuth electrode (where $1\ Cl^-$ is destroyed by the electrode process).

For ΔH in the general Gibbs-Helmholtz equation we must therefore substitute $\Delta H_D + \frac{3T_H K}{1+K}\,\Delta H_S$. The numerical equations corresponding to the two sets of measurements recorded in Table VII then become:

$$\left(\Delta H_D - (3 \times 0.0099 \times 6440)\right)\left(\frac{20}{308.1 \times 288.1}\right) + \left(3 \times 6440 \times 9.76 \times 10^{-22} \times {}^1/_7\,(308.1^7 - 288.1^7)\right) = \frac{3 \times 96500}{4.182}\left(\frac{-0.04063}{308.1} - \frac{-0.03636}{288.1}\right).$$

$$\left(\Delta H_D - (3 \times 0.0099 \times 6440)\right)\left(\frac{50}{323.1 \times 273.1}\right) + \left(3 \times 6440 \times 9.76 \times 10^{-22} \times {}^1/_7\,(323.1^7 - 273.1^7)\right) = \frac{3 \times 96500}{4.182}\left(\frac{-0.04425}{323.1} - \frac{-0.03369}{273.1}\right).$$

The values of ΔH_D corresponding to these two equations are —2730 and —2678 cal., while that derived above from the measurements with the hydrogen-bismuth and hydrogen-copper electrodes is —3070 cal. The mean of these three values is —2825 cal.; and we may write the following final thermochemical equation:

$$\mathrm{Bi\,(s)} + 3\mathrm{CuCl\,(s)} + \mathrm{H_2O} = 3\mathrm{Cu\,(s)} + \mathrm{BiOCl\,(s)} + 2\mathrm{H^+Cl^-\,(in\,\infty\,Aq)} + 2825\ \mathrm{cal.}$$

6. The Equilibrium Measurements.

Preliminary Experiments by F. H. Smyth.—Preliminary experiments on the equilibrium of the above mentioned reaction at 25° were made in this laboratory by Dr. F. H. Smyth, who shook together a mixture of bismuth, copper, bismuth oxychloride, cuprous chloride, and hydrochloric acid solutions of various concentrations, and analyzed the resulting solution after a lapse of time. He found that the reaction proceeded with such slowness in either direction that he was able to fix the equilibrium conditions only

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within wide limits; but by approaching the equilibrium from both sides, he determined that the substances are in equilibrium with one another at 25° when the acid concentration is somewhere between 0.50 and 0.20 molal. In his experiments there was this large divergence, even though the time allowed for the attainment of equilibrium was 3 months.

To determine the equilibrium conditions with any degree of accuracy, it is therefore necessary to make experiments at a higher temperature. The rate of the reaction can also be increased by providing a large surface of all the solids and by stirring effectively. All these means were employed simultaneously in the present investigation, in which the experiments were made at 75°.

Apparatus and Materials.—The apparatus used for the equilibrium measurements consisted of a round-bottomed glass tube 26 cm. long and 5 cm. in diameter, closed by a 4-hole rubber stopper, and containing a glass stirrer of propeller form and a conductivity cell. The shaft of the motor-driven stirrer passes through a gas-tight mercury seal. The conductivity cell was of the plunge-type. The conductivity measurement served to show the changes in concentration of the hydrochloric acid, and hence the progress of the reaction towards equilibrium.

The substances employed in the equilibrium measurements were prepared in the same way as for the equilibrium measurements, as described in Section 2 above.

Experimental Method.—The apparatus was set up in a thermostat at 75°; the reacting substances were introduced into the reaction bottle, which, to avoid oxidation, was filled with carbon dioxide gas; and the stirrer was started. The concentration of the hydrochloric acid in the solution was determined at intervals by means of the conductivity cell and bridge. The conductance in the apparatus at 75° of hydrochloric acid solutions of different concentrations had been previously determined. The cell was immersed in the solution only during the conductivity measurements. It was possible to detect a change in the hydrochloric acid concentration of 0.002 *M*.

When the conductance measurements indicated that the acid concentration was no longer changing, the stirring was stopped, and a 200 cc. portion of the solution was withdrawn through a glass-wool filter tube. This portion was analyzed for its content in chlorine, copper, and bismuth as follows: The chloride was determined in 25 cc. portions by adding nitric acid and silver nitrate, and weighing the silver chloride in perforated crucibles upon asbestos felt. The bismuth was determined in two 100 cc. portions by evaporating them with nitric acid till all chloride was expelled, dissolving the residue in dilute nitric acid, adding ammonium hydroxide and carbonate, filtering out the bismuth oxycarbonate in alundum crucibles, igniting, and weighing the bismuth oxide. The copper was determined

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by depositing it electrolytically directly out of the ammoniacal filtrate.

The Experimental Data.—Two preliminary experiments were first made to determine by the conductance measurements the rate of the reaction and roughly the position of the equilibrium at 75°. In these experiments the acid concentrations, which were initially 0.20 and 0.40 *M*, had become, after 72 hours, 0.275 and 0.372 *M*, respectively. A third experiment was then made, starting with 0.273 *M* acid. The concentration became 0.302 after 50 hours and 0.316 *M* after 180 hours. Sample No. 1 was then taken for analysis. In a fourth experiment the acid concentration was 0.386 at the start and 0.325 after 340 hours, when sample No. 2 was taken for analysis. A fifth, more complete experiment was then made. A mixture of 10 g. BiOCl, 5 g. CuCl, 35 g. Bi, 20 g. Cu, and 300 cc. 0.40 molal HCl were put into the reaction bottle. The concentration as indicated by the conductance measurements changed as follows:

Total hours.....	0	3	100	200	400	500	570
HCl concentration	0.386	0.378	0.350	0.335	0.319	0.314	0.312

A 200 cc. sample (No. 3) was then withdrawn and analyzed. To the equilibrium mixture 180 cc. HCl solution were then added, so as to bring its concentration to 0.291 molal. The concentration on continued stirring changed as follows:

Total hours.....	0	6	80	130	190	240
HCl concentration.....	0.291	0.295	0.309	0.312	0.314	0.314

Sample No. 4 was then withdrawn for analysis.

The results of the analyses of these samples are shown in Table IX. The figures for hydrogen are obtained by subtracting from the total chlorine concentration the chlorine combined with the bismuth (as $BiCl_3$) and with the copper (as CuCl). The concentrations are all expressed in mols per 1000 g. water.

TABLE IX.—ANALYSES OF THE EQUILIBRIUM SOLUTIONS AT 75°.

Sample No.	Concentration in mols per 1000 g. water.			
	Chlorine.	Copper.	Bismuth.	Hydrogen.
1.....	0.4059	0.0762	0.0033	0.3198
2.....	0.4186	0.0781	0.0044	0.3273
Average.....	0.4172	0.0772	0.0039	0.3236
3.....	0.4087	0.0769	0.00225	0.3251
4.....	0.4079	0.0765	0.00196	0.3255
Average....	0.4083	0.0767	0.00206	0.3253

It will be seen from the table that equilibrium was not reached in the preliminary experiments, since Samples 1 and 2 show considerable differences in composition. In the final experiments, however, it was, practically attained, since Samples 3 and 4 gave on analysis closely concordant results. As final values the averages given in the last line of the table will be adopted.

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7. Calculation of the Equilibrium Constants at 75°.

The equilibrium constant K of the reaction $Bi + 3CuCl + H_2O = 2H^+Cl^- + BiOCl + 3Cu$ is evidently expressed by the equation $(H^+)^2 \times (Cl^-)^2 = K$, since the chemical activities of all the substances except the hydrogen ion and chloride ion are constant. The hydrogen-ion concentration (H^+) in the solution is the sum of that produced by the ionization of the H^+Cl^- existing as such, by the ionization of the complex acid $H^+CuCl_2^-$ formed by the CuCl dissolved in the acid, and by the ionization of the complex acid $H^+_2BiCl_5^-$ formed by the BiOCl dissolved in the acid. The formation of these two complex acids has been shown by Bodländer and Storbeck[1] and by Noyes, Hall, and Beattie,[2] respectively. Assuming the 3 acids in the solution to have the same ionization-coefficient as pure hydrochloric acid at the same temperature and total concentration, the value of (H^+) is found by multiplying the hydrogen concentration (0.3253) given in the last line of the last column of Table I, by this ionization-coefficient.

The chloride-ion concentration (Cl^-) is found by multiplying by this same coefficient the concentration of the uncombined HCl, which itself is equal to the total chlorine diminished by twice the copper and five times the bismuth concentration. In the equilibrium solution the uncombined HCl has the concentration 0.2446 M (equal to $0.4083 - (2 \times 0.0767) - (5 \times 0.00206)$).

For the ionization-coefficient of the hydrochloric acid we have employed its activity-coefficient as derived by Noyes and Ellis[3] from electromotive-force measurements. They computed the activity-coefficient for 0.325 M hydrochloric acid to be 0.779 at 15° and 0.772 at 35°. Provided it continues to decrease at the same rate up to 75°, its value at 75° and 0.325 M would be 0.760.

The equilibrium constant at 75° is then given by the equation

$$K_{75} = (H^+)^5 \times (Cl^-)^2 = (0.3253 \times 0.76)^2 \times (0.2446 \times 0.76)^2 = 2.10 \times 10^{-3}.$$

8. Thermochemical Measurements of the Bismuth-Copper Reaction.

Data Available.—The data available for calculating the heat-effect attending the bismuth-copper reaction are the directly measured value of Thomsen[4] (—98,500 cal.) for the heat of formation of 1BiOCl (s) + 2HCl (in ∞ Aq) and the indirectly derived values of Thomsen and of Berthelot[5] (—98,700 and —106,200 cal.) for the heat of formation of 3CuCl (s). The difference between these values (+200 or +7700 cal.) should represent the increase in heat-content attending the reaction under consideration. But since this difference is derived from two much larger quantities,

[1] *Z. anorg. Chem.*, **26**, 361 (1901).

[2] THIS JOURNAL, **39**, 2532 (1917).

[3] *Ibid.*, 2543 (1917).

[4] Thomsen's *Thermochemische Untersuchungen*, **2**, 336 (1882).

[5] Berthelot's *Thermochimie*, **2**, 318 (1897); *Ann. chim. phys.*, [5] **20**, 514 (1880).

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and since for one of these quantities the two available determinations are discordant, no reliance can be placed on the result. We have therefore undertaken a more direct determination of the heat-effect attending the reaction.

Plan of the New Determinations.—The reaction itself not only proceeds too slowly to permit of its heat effect being measured calorimetrically, but it does not go nearly to completion. In consequence, the plan adopted was to use an auxiliary metal which would displace both bismuth and copper from their chlorides rapidly and completely. Tin was chosen because it fulfils these requirements, and because it is not appreciably acted upon by the dilute hydrochloric acid solution, in presence of which the reactions were carried out. Calorimetric measurements were therefore made of the heat changes at 25° attending the two reactions

$$3CuCl\,(s) + 1.5\,Sn\,(s) = 1.5\,SnCl_2\,(\text{in } 0.3\,M\,HCl) + 3Cu\,(s).$$

$$BiOCl\,(s) + 1.5\,Sn\,(s) + 2\,HCl\,(0.3\,M) = 1.5\,SnCl_2\,(\text{in } 0.3\,M\,HCl) + H_2O + Bi\,(s).$$

By subtraction is found the heat-content change at 25° attending the reaction

$$3CuCl\,(s) + Bi\,(s) + H_2O = 2HCl\,(0.3\,M) + BiOCl\,(s) + 3Cu\,(s).$$

The Apparatus and Materials.—The apparatus consisted of a Dewar tube of 6 cm. internal diameter and 22 cm. in length, in which were placed a vertical glass stirrer, a Beckmann thermometer, a second thermometer for measuring the temperature of the gas space above the hydrochloric acid with which the lower half of the Dewar tube was filled, and 2 baskets, one above the other, for holding 2 separate portions of the tin threads.

The bottom of the baskets was made of a hard rubber circular disk with a large hole in the center (through which the Beckmann thermometer passed) and with a large number of small holes to permit circulation of the liquid. The sides of the baskets consisted of a circular row of small vertical glass rods set into holes along the rim of the hard rubber disk. An inner concentric row of vertical glass tubes 25 cm. high was also set into the rubber disk around the central hole, thus making an annular space, in which the tin was placed. Each basket was separately supported by 2 long glass tubes set into the bottom of the basket and extending through the hard rubber cover of the Dewar tube. The 2 baskets could thus be successively pushed down into the solution.

The substances used were the same as before, except for the tin, which was pure block tin turned out into very fine threads in a lathe so as to afford the maximum possible surface.

The Experimental Procedure.—The experimental procedure varied according to whether bismuthoxychloride or cuprous chloride was under investigation. For a determination of the heat of reaction of bismuth-

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oxychloride with tin in hydrochloric acid solution, 303 g. of water were put into the Dewar tube from a pipet, the gas space above this water was filled with carbon dioxide, and then 102.91 g. of an approximately 1.5 *M* hydrochloric acid solution (nearly saturated with bismuthoxychloride at 25°) containing exactly 3.741 g. Bi[1] was added from another pipet. This resulted in the formation in the Dewar tube of 4.666 g. of finely divided solid bismuthoxychloride, suspended in about 400 cc. of 0.336 *M* hydrochloric acid solution containing a negligible quantity of dissolved bismuth. This procedure has the advantages that the bismuthoxychloride produced is free from basic compounds, and is in so finely divided a state as to react very rapidly with tin.

The cover of the Dewar tube was then placed in position with the upper and lower baskets filled with known weights of tin threads, and with the 2 thermometers in place, the Beckmann thermometer dipping into the solution, the other thermometer into the gas space. The 2 baskets of tin were suspended above the solution. The room temperature was kept within 1° of 25° during the experiment, so as to make the reaction nearly adiabatic. Carbon dioxide gas was passed into the Dewar tube to displace the air among the tin turnings; and, after waiting for a few minutes to allow the gas space above the solution to come to the same temperature, stirring of the solution was commenced, and the Beckmann thermometer was read every minute for 5 or 10 minutes, or until it showed a constant rate of temperature rise. The Beckmann thermometer used had been compared with a standardized Baudin thermometer. Care was taken to tap it vigorously before each reading.

The lower basket of tin was then introduced into the solution, it being raised and lowered gently during the rest of the experiment to furnish stirring. The Beckmann thermometer showed a rapid rise of temperature, which continued for about 7 minutes. At the end of this time the second basket of tin was lowered into the solution to hasten the reaction. After 3 minutes more the rise of temperature had practically ceased, but readings of the thermometer were taken for about 5 minutes more. This completed the experiment.

The use of 2 baskets of tin turnings introduced successively into the solution rendered the end point of the reaction much sharper, and contributed much to the accuracy of the determination.

To make sure that all the bismuthoxychloride had been reduced to bismuth, titrations with iodine solutions were made in 3 of the experiments to ascertain the amount of stannous chloride produced by the reaction, precautions being taken to prevent any oxidation of the stannous chloride during titration. In no case was the amount of stannous chloride pro-

[1] 52.90 g. of this solution yielded in 2 analyses 2.144 g. and 2.146 g. Bi_2O_3.

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duced found to be different by more than 0.4% from the amount of bismuthoxychloride introduced into the calorimeter.

In the experiments with cuprous chloride the above procedure required modification, since the solubility of cuprous chloride in hydrochloric acid is not sufficient to enable the production of the requisite quantity of solid cuprous chloride in the Dewar tube, and since the tendency of moist cuprous chloride to oxidize is very great. The method adopted was as follows:

A weighing tube was filled with a weighed amount of dry cuprous chloride (prepared free from cupric chloride, as proved by testing it with potassium iodide starch solution, by washing precipitated cuprous chloride with glacial acetic acid and drying in the air at 100°); and then, after all was in readiness, this cuprous chloride was poured from the tube into 375 cc. of 0.28 *M* hydrochloric acid contained in the Dewar tube and covered with an atmosphere of carbon dioxide gas. After the calorimeter and contents had come to constant temperature, the experiment was proceeded with exactly as described above for bismuthoxychloride. With cuprous chloride the reaction proceeded much more rapidly than with bismuthoxychloride, and was completed within 7 minutes, even though both baskets of tin were introduced at the same time. The solution was analyzed for stannous chloride as before; and the amount formed was always found equivalent within 0.4% to the amount of cuprous chloride taken.

The observed temperature rises were in each case corrected for heat radiation in the usual manner. The heat effects to which they corresponded were calculated with the aid of data on the heat capacity of the different systems used. These heat data were obtained in independent experiments in which a nearly equal rise of temperature was produced in a system nearly identical with that used above by the introduction of a measured amount of electrical energy. The only differences between the systems used in the measurements of the heat of reaction and in the determinations of the heat capacity were the presence in the latter system of a small heating coil of enamelled resistance wire and the absence of the cuprous chloride. These small differences were corrected for with the aid of data on the specific heat capacities of tin, cuprous chloride, and the resistance wire,—data which need be only approximately accurate.

The quantity of heat introduced electrically in the heat-capacity experiments was determined by measurements of the resistance at 25° of the heating coil, of the potential difference (12 volts) applied by a storage battery to the terminals of this resistance (20.53 ohms) and of the time of application (about 15 minutes). The resistance was measured to 0.1% by means of a Wheatstone's bridge, the voltage to 0.01 volt by means of a calibrated Weston voltmeter, and the time to a fraction of a second by means of a watch.

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The Experimental Data.—Typical sets of data for a determination with bismuthoxychloride, for one with cuprous chloride, and for one of the heat capacity of the system used in an experiment with bismuthoxychloride are given in Table X.

TABLE X.—TYPICAL EXPERIMENTAL DATA FOR THE HEAT OF REACTION MEASUREMENTS.

Time in min.	Thermometer readings in experiments on		
	BiOCl.	CuCl.	Heat capacity.
0	0.141	0.754	0.212
1	0.140	0.756	0.219
2	0.140	0.757	0.227
3	0.140	0.759	0.233
4	0.140	0.760	0.239
5	0.140[1]	0.762	0.245
6	0.270	0.764	0.251
7	0.470	0.766[1]	0.257
8	0.635	1.140	0.450[3]
9	0.755[2]	1.510	0.665
10	0.840	1.650[2]	0.880
11	0.940	2.010	1.110
12	1.010	2.035	1.335
13	1.040	2.054	1.560
14	1.050	2.077	1.775
15	1.055	2.084	1.990
16	1.057	2.091	2.205
17	1.059	2.098	2.420
18	1.061	2.105	2.640
19	1.063	2.112	2.860
20	1.065	2.118	3.080
21	1.067	.....	3.295
22	.....	.....	3.510
23	.....	.....	3.725
24	.....	.....	3.940
25	.....	.....	4.155[4]
26	.....	.....	4.367
27	.....	.....	4.360
28	.....	.....	4.354

These data show the immediate evolution of heat when the first basket of tin was lowered, and the increase in rate of reaction caused by lowering the second basket. They indicate that the reaction was practically complete after 10 minutes in the case of the bismuth experiments, and after 7 minutes in the case of the copper experiments. They show also the rate of temperature change before and after the reaction.

Six experiments similar to the above were made upon bismuthoxychlo-

[1] First basket lowered.
[2] Second basket lowered.
[3] Current turned on.
[4] Current turned off.

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TABLE XI.—EXPERIMENTAL DATA ON THE HEAT OF REACTION OF BISMUTHOXYCHLORIDE AND TIN IN HYDROCHLORIC ACID SOLUTION.

Experiment No.	I.	II.	III.	IV.	V.	VI.
Mols BiOCl used	0.01798	0.01798	0.01798	0.01798	0.01798	0.01798
Mols HCl per 1000 g. H_2O — Initial	0.336	0.336	0.336	0.336	0.336	0.336
Mols HCl per 1000 g. H_2O — Final	0.246	0.246	0.246	0.246	0.246	0.246
Grams of tin	35.48	45.09	41.40	30.06	44.80	42.88
Initial thermometer reading	0.133	0.140	0.789	1.810	0.945	1.476
Final thermometer reading	1.038	1.053	1.681	2.716	1.924	2.426
Radiation correction	+0.009	—0.009	—0.002	—0.006	—0.033	—0.040
Corrected temperature rise	0.914	0.904	0.890	0.900	0.946	0.910
Temperature of solution	24.10	23.06	23.29	24.31	23.45	23.98
Temperature of baskets	24.22	23.05	23.02	24.19	24.60	24.20
Heat capacity of baskets	13.5	13.5	13.5	13.5	13.5	13.5
Heat capacity of Tin	2.0	2.5	2.3	1.7	2.5	2.4
Total heat capacity	437.8	438.3	438.1	437.6	438.3	438.2
Calories evolved	400.1	396.3	390.1	393.9	414.7	398.8
Heat introduced by baskets	1.8	0.0	4.3	1.9	1.6	3.5
Calories evolved (corrected)	398.3	396.3	394.4	395.8	396.3	395.3
Calories per mol BiOCl	22150	22047	21930	22010	22090	21990

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TABLE XII.—EXPERIMENTAL DATA ON THE HEAT OF REACTION OF CUPROUS CHLORIDE AND TIN IN HYDROCHLORIC ACID SOLUTION.

Experiment No.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Grams CuCl used	5.7674	4.8670	4.6809	4.4557	4.8610	4.5547	4.7343	4.6882
Mols CuCl used	0.05824	0.04915	0.04727	0.04499	0.04909	0.04599	0.04781	0.04734
Mols HCl per 1000 g. H_2O	0.278	0.278	0.278	0.278	0.278	0.278	0.278	0.248
Grams of tin	38.38	46.96	47.82	52.08	55.55	58.93	60.63	50.61
Initial thermometer reading	0.411	0.766	0.483	0.230	0.503	0.676	0.510	0.397
Final thermometer reading	1.958	2.077	1.784	1.422	1.800	1.944	1.779	1.669
Radiation correction	—0.026	—0.030	—0.024	—0.011	—0.017	—0.040	—0.021	—0.024
Corrected temperature rise	1.512	1.281	1.277	1.181	1.280	1.228	1.248	1.248
Temperature of solution	24.79	25.15	24.86	24.61	24.88	25.06	24.89	24.78
Temperature of baskets	24.81	25.30	26.00	25.04	24.95	25.88	25.08	25.20
Heat capacity of baskets	13.5	13.5	13.5	13.5	13.5	13.5	13.5	13.5
Heat capacity of tin	2.14	2.61	2.66	2.90	3.09	3.28	3.38	2.87
Heat capacity of CuCl	0.80	0.67	0.65	0.62	0.67	0.62	0.65	0.65
Total heat capacity	41.03	410.37	410.40	410.61	410.85	410.99	411.11	410.61
Calories evolved	623.66	525.68	524.08	484.93	525.89	504.70	513.07	512.44
Heat introduced by baskets	0.03	2.52	19.15	7.31	1.21	13.75	3.34	7.14
Correction for heat of solution of CuCl	—41.6	—41.6	—41.6	—41.6	—41.6	—41.6	—41.6	—41.6
Calories evolved (corrected)	582.0	481.6	463.3	436.0	483.1	449.3	468.1	463.7
Calories per mol CuCl	9990	9800	9780	9690	9860	9770	9790	9800

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ride, 8 on cuprous chloride, 3 for determining the heat capacity of the bismuth system, and 5 for the heat capacity of the copper system.

The 3 determinations of the heat capacity of the bismuth system resulted in the figures 436.06, 436.04, and 435.70 calories per degree, for a temperature of 25°. The average of these is 435.93 calories per degree; but from this is to be subtracted the heat capacity of the resistance coil (0.13), leaving 435.80 calories per degree. To this figure is to be added the heat capacity of the quantity of tin used in the baskets in any particular experiment, giving the heat capacity of the bismuth system in that experiment.

The 5 determinations of the heat capacity of the copper system resulted in the figures 407.10, 407.27, 407.28, 407.13, and 407.28 calories per degree, the average being 407.29. Subtracting 0.13 as before, we get 407.16 calories per degree, a figure to which must be added the heat capacities of the tin and of the cuprous chloride used in a given reaction experiment.

The results of the 6 experiments on bismuthoxychloride are given in Table XI; these of the 8 experiments on cuprous chloride in Table XII.

9. The Heat Effect Attending the Bismuth-Copper Reaction.

The mean value given by the above experimental data for the heat evolved at 25° when 1 mol of bismuthoxychloride reacts with tin and hydrochloric acid of concentration about 0.3 *M* is 22040 (a. d. 60) calories, and that for the heat evolved when 1 mol of cuprous chloride reacts with tin and hydrochloric acid of the same concentration is 9810 (a. d. 60) calories. By combining these two results we get for the reaction whose equilibrium we studied the following equation expressing the heat effect at 25°:

$$\mathrm{Bi\,(s) + 3CuCl + H_2O =}$$
$$\mathrm{BiOCl\,(s) + 3Cu\,(s) + 2HCl\,(0.3\ mol.) + 7390\ cal.}$$

This result is different by 4565 cal. from the value (2825 cal.) derived in Section 5 from the electromotive-force measurements. As a careful consideration of the measurements makes it seem improbable that either of these results can be in error by even 500 cal., we are entirely unable to account for the discrepancy.

10. The Equilibrium Constant at 25° and the Corresponding Difference in the Two Specific Electrode Potentials.

The equilibrium constant at 25° (K_{298}) can be computed from that at 75° (K_{348} = 0.00210) and the increase in heat content ΔH by the equation

$$2.303 \log_{10} \frac{K_{298}}{K_{348}} = \frac{\Delta H}{1.989}\left(\frac{1}{348.1} - \frac{1}{298.1}\right).$$

According as we adopt the value of ΔH derived from the electromotive forces (—2825 cal.) or that derived from the heat measurements (—7390 cal.), we find at 25° for the equilibrium constant K_{298}, equal to $(H^+)^2 \times$

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$(Cl^-)^2$, the value 0.00416 or the value 0.0126, corresponding to an equilibrium concentration of ionized hydrochloric acid of 0.254 M or of 0.335 M.

From these values of K we may calculate the difference in the two specific potentials by means of the equation

$$\bar{E}_{BiOCl} - \bar{E}_{CuCl} = \frac{RT}{3F} \log K = 0.01972 \log_{10} K.$$

The difference in the two potentials is thus found to be —0.0469 volt or —0.0375 volt at 25°. The value derived directly from the electromotive forces, as given in Table VIII was —0.0401 volt, thus intermediate between the 2 values derived from the equilibrium measurements with the aid of the 2 independently determined heat effects. Incidentally it indicates that the true heat effect may be intermediate between the 2 values.

11. Summary.

In this research the specific or normal potentials at 15 ,25, and 35° of the electrodes $\left.\begin{matrix}Bi\\BiOCl\end{matrix}\right\}, \begin{matrix}H^+\\Cl^-\end{matrix}$ and $\left.\begin{matrix}Cu\\CuCl\end{matrix}\right\}, Cl^-$ have been derived from measurements of cells formed by combining these electrodes separately with a hydrogen electrode (H_2, H^+) and with each other. The final results will be found in Table VIII.

From the change of the electrode potentials with the temperature the corresponding heat effects at 25° have been computed, and found to be those expressed by the following equations:

$$^3/_2H_2\,(g) + 3CuCl\,(s) = 3Cu\,(s) + 3H^+Cl^-\,(\text{in } \infty\ Aq) + 21{,}570 \text{ cal.}$$

$$^3/_2H_2\,(g) + BiOCl\,(s) = Bi\,(s) + H_2O + H^+Cl^-\,(\text{in } \infty\ Aq) + 18{,}500 \text{ cal.}$$

$$Bi\,(s) + 3CuCl\,(s) + H_2O\,(l) = 3Cu\,(s) + 2H^+Cl^-\,(\text{in } \infty\ Aq) + 2825 \text{ cal.}$$

The heat effect attending the last of these reactions was also determined by thermochemical methods, allowing metallic tin to act in one case on cuprous chloride and in another case on bismuthoxychloride, in the presence of dilute hydrochloric acid. The value found (7390 cal.) differs considerably from that (2825 cal.) derived from the electromotive-force measurements—a discrepancy that can not be at present accounted for.

The equilibrium condition of the last of these reactions was determined at 75° by preparing and analyzing an equilibrium mixture. The equilibrium constant, equal to $(H^+)^2 \times (Cl^-)^2$, was found to be 0.0021 at 75°. Its value at 25°, calculated with the aid of the heat effect, is shown to accord fairly well with the difference between the 2 specific electrode potentials derived from the electromotive-force measurements.

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[CONTRIBUTION FROM THE LABORATORY OF THE GEORGE WASHINGTON UNIVERSITY.]

A CONFIRMATION OF VAN'T HOFF'S HYPOTHESIS. OPTICAL SUPERPOSITION IN THE METASACCHARINS AND RELATED BODIES.

BY EDWIN A. HILL.

Received February 7, 1918.

Van't Hoff's hypothesis, or the so-called principle of optical superposition, states that the specific rotation of an optically active substance is the algebraic sum of certain constants corresponding to the active atoms present.

The early work of Guye, Gautier and Walden, was supposed to afford experimental proof of the validity of this proposition,[1] but Rosanoff[2] and others have claimed to show, that owing to "serious errors in principle" involved in the experimental work, these results in reality prove nothing either for or against the theory, and more recently Patterson,[3] in a series of 4 articles, has concluded "that the experiments of Guye and Walden have in reality no bearing on the matter in hand, and that the validity of Van't Hoff's hypothesis is distinctly open to doubt."

On the other hand the series of articles by Dr. C. S. Hudson[4] which have appeared in THIS JOURNAL from time to time, indicate that the principle does hold, at least approximately, in certain cases, for as he has remarked[5] it is otherwise quite unlikely that the simple numerical relations disclosed by him could exist.

The problem may be more specifically stated as follows: The formula for *l*-arabinose is sometimes written as given below, with an aldehyde group at the end of the chain, indicating the presence of three active carbon atoms denoted by α, β and γ, respectively, so that the specific rotation of the molecule is the algebraic sum of the rotations of the active carbons α, β and γ.

$$\begin{array}{ccccccc} & OH & & OH & & H & \\ HOCH_2 - & C & - & C & - & C & - COH. \\ & H & & H & & OH & \\ & \gamma & & \beta & & \alpha & \end{array}$$

The disputed question is what will be the effect upon either the sign or the numerical value of the activity of any of these atoms, *e. g.*, the α carbon if we allow the H and OH attached to any one of the other carbons, *e. g.*, the β or γ carbon, to exchange places?

Van't Hoff's hypothesis predicates that there will be no change whatever, in either the sign or the magnitude of the activity of the α carbon; those like Rosanoff and Patterson, who question the validity of the hypo-

[1] See Landolt, "Opt. Rot. of Org. Substances," pp. 296–298.

[2] THIS JOURNAL, **28**, 525 (1906); **29**, 536 (1907).

[3] *J. Chem. Soc.*, **87**, 33 (1905); **89**, 1885 (1906); **91**, 705 (1907); **107**, 142 (1915).

[4] THIS JOURNAL, **31**, 66–86 (1909); **32**, 338–346 (1910); as also later articles.

[5] *Ibid.*, **31**, 68 (1909), footnote.

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thesis, assert the possibility of a change in either the sign or numerical value or perhaps both of the activity of the α carbon under these circumstances.

In the above formula with three active carbons present, the theory requires the existence of 4 isomers, each having a different value of $[\alpha]_D$, and there are in fact 4 known pentose sugars, of which arabinose above-mentioned is one, the other 3 being, respectively, ribose, xylose and lyxose.

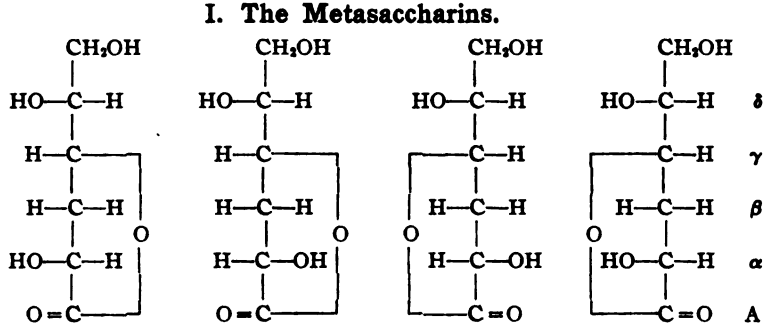
It would seem simple enough to let α, β and γ represent the numerical values of the supposed constants, calling their signs + when H is above the chain and — when below it, and so to form 4 independent equations by using the value of $[\alpha]_D$ as determined for each sugar.

Then 3 of these equations could be used for determining the values of the constants, and if these values, when substituted in the fourth equation satisfied it within the limits of experimental error, the proposition would be fully established.

This method however fails when applied to the values of $[\alpha]_D$ for stable solutions of this group of sugars, for the fact that these sugars display mutarotation, is now generally held to indicate the presence of 4, instead of 3 active atoms, and so to render the method inapplicable for lack of sufficient data.

And so with reference to all groups of isomers to which this method of proof can be applied, it will usually be found that we lack a sufficient number of determinations of $[\alpha]_D$ to compute the constants, and properly verify the values so computed, so that so far as the writer is advised, no case has yet been presented in which the values of all of the supposed constants can be computed, and then verified by the values of $[\alpha]_D$ not used in computing the constants, the values of $[\alpha]_D$ being for pure crystalline substances.

I. The Metasaccharins.



	α,δ-Galacto-metasaccharin. (I).	β,δ-Galacto-metasaccharin. (II).	β-Dextro-metasaccharin. (III).	α-Dextro-metasaccharin. (IV).
$[\alpha]_D^{20}$ =	—45.3°	—62.96°	+8.2°	+25.28°
M. p. =	144°	55 to 60°	92°	104°

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The writer therefore presents herewith the cases of the 4 metasaccharins and their salts, in which the principle of optical superposition holds very closely, and to which he believes attention has never yet been called.

The formulas and data for these bodies will be found collected by Browne in his handbook of Sugar Analysis, p. 587 and 604. They were prepared by Nef,[1] and the constants determined by him.

In these bodies only the α, γ and δ carbons are active, and the values of the 3 constants can therefore be computed from the values of $[\alpha]_D^{20}$ for the first 3 bodies, and from these constants the value of $[\alpha]_D^{20}$ for the fourth body can be computed, with a variation from the observed value less than the limit of experimental error, thus proving the principle for this set of isomers.

Thus let α, γ and δ be the constants of the α, γ and δ carbons, then by Van't Hoff's principle we shall have for any one of these bodies

$$[\alpha]_D^{20} = \pm\alpha \pm \gamma \pm \delta.$$

For any particular body I shall, for vertically written formulas, give the constants the + sign when the H atom is on the right hand, and the — sign when on the left hand of the vertical chain, the A carbon being at the bottom we then have available these equations.

From α,δ-galacto metasaccharin	$[\alpha]_D^{20} = +\alpha - \gamma + \delta = 45.3°$[2]	(1)
From β,δ-galacto metasaccharin	$[\alpha]_D^{20} = -\alpha - \gamma + \delta = -62.96$[2]	(2)
From β-dextro metasaccharin	$[\alpha]_D^{20} = -\alpha + \gamma + \delta = +8.2$[3]	(3)
From α-dextro metasaccharin	$[\alpha]_D^{20} = +\alpha + \gamma + \delta = +25.28$[3]	(4)

We can select any 3 of these equations, and having determined the constants therefrom, insert their values in the fourth equation, and thereby compute the value of $[\alpha]_D^{20}$. Thus using the first three equations, the values of the constants are as follows:

Subtracting Equation 2 from 1 gives $2\alpha = +17.66$, and $\alpha = +8.83°$
Subtracting Equation 3 from 2 gives $-2\gamma = -71.16$, and $\gamma = +35.58$
Adding 1 to 3 gives $2\delta = -37.10$, and $\delta = -18.55$

Substituting in Equation 4:

$$[\alpha]_D^{20} = +8.83 + 35.58 - 18.55 = 25.86° \text{ computed}$$
$$25.28 \text{ observed}$$
$$-0.58 \text{ difference}$$

This fully establishes the principle.

Recomputation of the Constants.

By using all 4 of the observed values of $[\alpha]_D^{20}$, and giving each observation an equal weight, so as to distribute the errors of observation more equally between the values of the constants, we obtain the following values for the

[1] *Ann.*, 376, 1 (1910).
[2] Browne, p. 604.
[3] Browne, p. 587; citing Nef, *Ann.*, 376, 1 (1910).

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three constants, specific rotations being stated to the nearest tenth of a degree.

CONSTANTS OF THE METASACCHARINS.

Rotations.	Values of the constant. α.	γ.	δ.
Specific rotations, H to the right	+8.9°	+35.5°	—18.8°
Molecular rotations, H to the right	+1426°	+5767°	—3046°

Using these values, we can compute the following table of specific rotations:

COMPUTED SPECIFIC ROTATIONS OF THE METASACCHARINS.

Bodies.	Signs of constants.	Equations.	Values of $[\alpha]_D^{20}$. Computed.	Observed.	Difference.
α,δ-Galactometasaccharin	$+\alpha-\gamma+\delta$	+8.9—35.5—18.8°	—45.4°	—45.3°	—0.10°
β,δ-Galactometasaccharin	$-\alpha-\gamma+\delta$	—8.9—35.5—18.8	—63.2	—62.96	—0.24
β-Dextrometasaccharin	$-\alpha+\gamma+\delta$	—8.9+35.5—18.8	+ 8.0	+ 8.20	—0.20
α-Dextrometasaccharin	$+\alpha+\gamma+\delta$	+8.9+35.5—18.8	+25.6	+25.28	+0.32

The agreement between computed and observed values, as shown by the differences in the last column, being well within the limit of experimental error.

The metasaccharins are in structure lactones of acids, and when they form salts, with organic bases they act as such, and must hence contain a carboxyl group, which is evidently formed by the opening of the ring, and the addition of a molecule of water, the hydroxyl of which attaches to the γ carbon, and the hydrogen to the oxygen of the broken ring, forming the carboxyl group.

The alkaloids strychnine, brucine and quinine are nitrogen bases, forming salts by addition instead of subtraction, the first two being monacid, and the latter diacid.

To what extent the lactonic ring is broken up and the corresponding acid formed, when a metasaccharin is dissolved in water, I am not advised. Neff,[1] who prepared these metasaccharins by the action of alkalies on different sugars, also prepared their strychnine, brucine and quinine salts and determined the values of $[\alpha]_D^{20}$ in aqueous solution for all of them.[2] By using these values it is found, that for each of these three bases, the 4 corresponding salts of the metasaccharins form a similar series, in which the principle of optical superposition also holds, as is shown below.

II. The Strychnine Salts of the Metasaccharin.

The formula for these bodies may be written

$$[\alpha]_D = \pm \alpha \pm \gamma \pm \delta \pm St.$$

Where St is the sum of the effects of the active atoms of the strychnine nucleus, giving us the following four equations:

[1] *Ann.*, 376, 1 (1910).
[2] *Loc. cit.*

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$[\alpha]_D^{20}$ FOR STRYCHNINE SALTS

α,δ-Galactometasaccharin	$= -8.41° = +\alpha - \gamma + \delta \pm St^1$	(5)
β,δ-Galactometasaccharin	$= -23.43 = -\alpha - \gamma + \delta \pm St^1$	(6)
α-Dextrometasaccharin	$= -19.50 = +\alpha + \gamma + \delta \pm St^1$	(7)
β-Dextrometasaccharin	$= -30.79 = -\alpha + \gamma + \delta \pm St^1$	(8)

Subtracting 6 from 5 gives $2\alpha = +15.02°$ and $\alpha = +7.51°$

Subtracting 7 from 5 gives $-2\gamma = +11.09$ and $\gamma = -5.55$

Adding 6 to 7 gives $2\delta \pm 2St = -42.93$ and $\delta \pm St = -21.47$

Substituting these values in Equation 8:

$$-\alpha + \gamma + \delta \pm St = -7.51 - 5.55 - 21.47 = -34.53 \text{ computed}$$
$$-30.79 \text{ observed}$$
$$-3.74 \text{ difference}$$

This is a difference which is within the limits of experimental error.

This difference, as before, can be distributed between the values of the 3 constants, by reducing each constant numerically by the quantity 0.93°, giving for the values of the constants for the strychnine salts as follows:

CONSTANTS FOR STRYCHNINE SALTS.

Rotations.	α.	γ.	$\delta \pm St$.
Specific rotation $[\alpha]_D^{20}$	+6.58°	−4.62°	−20.54°
Molecular rotation $[M]_D^{20}$	+3382	−2375	−10558

Using the above values of the constants for the specific rotation, we have the following table:

COMPUTED SPECIFIC ROTATIONS OF STRYCHNINE SALTS OF THE METASACCHARINS.

Bodies.	Signs of constants.	Equations.	Values of $[\alpha]_D^{20}$. Computed.	Observed.	Difference.
α,δ-Galactometasaccharin	$+\alpha-\gamma+\delta\pm St$	$+6.58+4.62-20.54$	−9.34°	−8.41°	−0.93°
β,δ-Galactometasaccharin	$-\alpha-\gamma+\delta\pm St$	$-6.58+4.62-20.54$	−22.50	−23.43	+0.93
α-Dextrometasaccharin	$+\alpha+\gamma+\delta\pm St$	$+6.58-4.62-20.54$	−18.58	−19.50	+0.92
β-Dextrometasaccharin	$-\alpha+\gamma+\delta\pm St$	$-6.58-4.62-20.54$	−31.74	−30.79	−0.95

Here again the agreement between the observed and computed values of $[\alpha]_D$ is good, and the principle is fully established.

III. The Brucine Salts of the Metasaccharins.

The formula for these bodies will be

$$[\alpha]_D = \pm \alpha \pm \gamma \pm \delta \pm Br.$$

Where as before Br is the sum of the constants for the active atoms of the brucine molecule, the 4 equations being:

$[\alpha]_D^{20}$ FOR BRUCINE SALTS.

α,δ-Galactometasaccharin	$= +\alpha - \gamma + \delta \pm Br = -12.74°$	(9)
β,δ-Galactometasaccharin	$= -\alpha - \gamma + \delta \pm Br = -25.20$	(10)
α-Dextrometasaccharin	$= +\alpha + \gamma + \delta \pm Br = -23.14$	(11)
β-Dextrometasaccharin	$= -\alpha + \gamma + \delta \pm Br = -33.14$	(12)

[1] Nef, *Ann.*, **376**, 74, 81, 98 and 97 (1910).

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The values of $[\alpha]_D^{20}$ are those given by Nef.[1] Following the method used for the strychnine salts, we can obtain from Equations 9, 10 and 11 the values $\alpha = +6.24°$, $\gamma = -5.2°$ and $(\delta \pm Br) = -24.18°$, whence by substitution in Equation 12 we have

$$-\alpha + \gamma + (\delta \pm Br) = -6.24 - 5.2 - 24.18 = -36.62° \text{ computed}$$
$$-34.14 \text{ observed}$$
$$-2.42 \text{ difference}$$

This is a difference which is not in excess of the experimental error, and which when distributed as before equally between the 4 observations, reduces the average difference to 0.62°, and gives us the following constants for the brucine salts:

CONSTANTS FOR BRUCINE SALTS.

Rotations.	α.	γ.	$\delta \pm$ Br.
Specific rotations $[\alpha]_D^{20}$	+5.62	−4.58	−23.56
Molecular rotations $[M]_D^{20}$	+3226	−2629	−13523

Then as before, using the corrected values of the constants for the specific rotation, we obtain the following table:

COMPUTED SPECIFIC ROTATIONS, BRUCINE SALTS OF METASACCHARINS

Bodies.	Signs of constants.	Equations.	Values of $[\alpha]_D^{20}$. Computed.	Observed.	Difference.
α,δ - Galactometasaccharin	$+\alpha-\gamma+(\delta\pm Br)$	+5.62+4.58−23.56	−13.36°	−12.74°	−0.62°
β,δ - Galactometasaccharin	$-\alpha-\gamma+(\delta\pm Br)$	−5.62+4.58−23.56	−24.60	−25.20	+0.60
α - Dextrometasaccharin	$+\alpha+\gamma+(\delta\pm Br)$	+5.62−4.58−23.56	−22.52	−23.14	+0.62
β - Dextrometasaccharin	$-\alpha+\gamma+(\delta\pm Br)$	−5.62−4.58−23.56	−33.76	−33.14	−0.62

Here is an agreement between observed and computed values which is even better than in the case of the strychnine salts.

IV. The Quinine Salts of the Metasaccharins.

The formula for these bodies will be

$$[\alpha]_D = \pm \alpha \pm \gamma \pm \delta \pm Qu$$

where as before Qu is the sum of the constants for the active atoms of the quinine molecule, the 4 equations being

$[\alpha]_D^{20}$ FOR QUININE SALTS.

α,δ-Galactometasaccharin	$= +\alpha - \gamma + \delta \pm Qu = -90.5°$	(13)
β,δ-Galactometasaccharin	$= -\alpha - \gamma + \delta \pm Qu = -104.1$	(14)
α-Dextrometasaccharin	$= +\alpha + \gamma + \delta \pm Qu = -100.9$	(15)
β-Dextrometasaccharin	$= -\alpha + \gamma + \delta \pm Qu = -113.6$	(16)

[1] *Loc. cit.*

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The values of $[\alpha]_D^{20}$ are those given by Nef.[1]

Then as before, from Equations 13, 14 and 15 we can obtain the values $\alpha = +6.8$, $\gamma = -5.2$ and $\delta \pm Qu = -90.5$.

Whence by substitution in Equation 16 we have

$$-\alpha + \gamma + (\delta \pm Qu) = -6.8 - 5.2 - 102.5 = -114.5 \text{ computed}$$
$$-113.6 \text{ observed}$$
$$-0.9 \text{ difference}$$

This is a very satisfactory proof of the application of the principle.

When this difference of $-0.9°$ is distributed between the 4 observations, we obtain the following values for the constants:

CONSTANTS FOR QUININE SALTS.

Rotation.	α.	γ.	$\delta \pm Qu$.
Specific rotation $[\alpha]_D^{20}$	+6.58°	−4.98°	−102.28°
Molecular rotation $[M]_D^{20}$	+3316	−2510	−51549

From which constants the following table is computed:

COMPUTED SPECIFIC ROTATIONS, QUININE SALTS OF METASACCHARINS.

Bodies.	Signs of constants.	Equations.	Values of $[\alpha]_D^{20}$. Computed.	Observed.	Difference.
α,δ - Galactometasaccharin	$+\alpha-\gamma+(\delta\pm Qu)$	$+6.58+4.98-102.28$	−90.72°	−90.50°	−0.22°
β,δ - Galactometasaccharin	$-\alpha-\gamma+(\delta\pm Qu)$	$-6.58+4.98-102.28$	−103.88	−104.10	+0.22
α - Dextrometasaccharin.....	$+\alpha+\gamma+(\delta\pm Qu)$	$+6.58-4.98-102.28$	−100.68	−100.90	+0.22
β - Dextrometasaccharin.....	$-\alpha+\gamma+(\delta\pm Qu)$	$-6.58-4.98-102.28$	−113.84	−113.60	−0.24

This shows exceedingly good agreement between computed and observed values.

Below will be found a comparative table of the constants of these metasaccharins and their salts.

COMPUTED CONSTANTS OF THE METASACCHARINS AND THEIR SALTS SPECIFIC AND MOLECULAR ROTATIONS.

Bodies.	Molecular weights. Base.	Total.	Specific rotations $[\alpha]_D$. α.	γ.	δ.	Molecular rotations $[M]_D$. α.	γ.	δ.
Metasaccharins.....	...	180	+8.8°	+35.6°	−18.8°	+1426°	+5767°	−3046°
Their salts.....	...	...	....	....	$\delta \pm \beta$	....	....	$\delta \pm \beta$
Strychnine.....	334	514	+6.58	−4.62	−20.54	+3382	−2375	−10588
Brucine.....	394	574	+5.62	−4.58	−23.56	+3226	−2629	−13523
Quinine acid salt.....	324	504	+6.58	−4.98	−102.28	+3316	−2510	−51549

As the molecular weights of the substances differ, because of the difference in the molecular weights of the 3 bases, we would not expect the values of the α and γ constants of specific rotation to agree. The molecular

[1] *Loc. cit.*

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rotation constants, however, should agree for the α and γ carbons, provided the various salts are all dissociated to an equal extent, for then the effect of the base would be fully eliminated by subtraction.

It will be noted, that the agreement between the three salts in the values of the molecular constants of the α and γ carbons, is quite good, the average for the α constant being $+3308°$, and for the γ constant $-2805°$. The departures from the average values being for the α constants, $+74°$, $+8°$ and -82, and for the γ constants, $+135°$, $-5°$ and $-119°$, which are less than $^1/_2$ degree of specific rotation in the α constant, and less than a single degree of such rotation in the γ constant, and may be considered well within the limit of experimental error.

The metasaccharins themselves are ring compounds while the salts are chains, and we therefore find as would be expected considerable difference in the values of the constants for the acids on the one hand, and for the salts on the other. The value of the δ constant in the case of the salts above, is tied up with the activity of the active base, but we have already found the following values, *viz.*:

$$\delta \pm \text{St} = -10558, \quad \delta \pm \text{Br} = -13523, \quad \delta \pm \text{Qu} = -51549$$

Now by using these molecular constants, with the constants for the α and γ carbons, and using the equations already established, the molecular and specific rotations of all of the 12 salts can be computed with very small departures from the observed values, as is shown in the following table:

SALTS OF THE METASACCHARINS. COMPUTATIONS OF MOLECULAR AND SPECIFIC ROTATIONS.

Bodies	Equation.	Molecular constants. α.	γ.	$\delta \pm \beta$.	Molecular rotation.	Specific rotations. Computed.	Observed.	Diff.
Strychnine Salts of the Metasaccharins M. W = 514.								
α,δ-Galacto	$+\alpha-\gamma+\delta\pm$St	+3308	+2505	−10558	−4745	− 9.23°	− 8.41°	−0.82
β,δ-Galacto	$-\alpha-\gamma+\delta\pm$St	−3308	+2505	−10558	−11361	− 22.10	− 23.43	+1.33
α-Dextro	$+\alpha+\gamma+\delta\pm$St	+3308	−2505	−10558	−9755	− 18.96	− 19.50	+0.54
β-Dextro	$-\alpha+\gamma+\delta\pm$St	−3308	−2505	−10558	−16371	− 31.85	− 30.79	−1.06
Brucine Salts of the Metasaccharins M. W = 574.								
α,δ-Galacto	$+\alpha-\gamma+\delta\pm$Br	+3308	+2505	−13523	−7710	− 13.43	− 13.36	−0.07
β,δ-Galacto	$-\alpha-\gamma+\delta\pm$Br	−3308	+2505	−13523	−14326	− 24.96	− 24.60	−0.36
α-Dextro	$+\alpha+\gamma+\delta\pm$Br	+3308	−2505	−13523	−12720	− 22.00	− 22.52	+0.52
β-Dextro	$-\alpha+\gamma+\delta\pm$Br	−3308	−2505	−13523	−19336	− 33.68	− 33.76	−0.08
Acid Quinine Salts of the Metasaccharins M. W. = 504.								
α,δ-Galacto	$+\alpha-\gamma+\delta\pm$Qu	+3308	+2505	−51549	−45736	− 90.74	− 90.50	−0.24
β,δ-Galacto	$-\alpha-\gamma+\delta\pm$Qu	−3308	+2505	−51549	−52352	−103.87	−104.10	+0.23
α-Dextro	$+\alpha+\gamma+\delta\pm$Qu	+3308	−2505	−51549	−50746	−100.68	−100.90	+0.22
β-Dextro	$-\alpha+\gamma+\delta\pm$Qu	−3308	−2505	−51549	−57362	−113.81	−113.60	−0.21
Algebraic sum of the differences								−0.16
Average departure								−0.47

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The Work of Dr. C. S. Hudson.

In view of the closeness of the application of Van't Hoff's principle to the metasaccharins and their salts, as has been already illustrated, I will briefly review the work of Dr. C. S. Hudson and his co-workers, which apparently indicates the application of the principle to various other groups of substances as well.

In 1909 Dr. Hudson[1] announced that the specific rotation of many sugars and their derivatives could be expressed by the equation $[\alpha]_D = B \pm A$ where A represented the rotation of the end asymmetric carbon, and B the algebraic sum of the rotations of the remaining active carbons present. In this and subsequent papers he proved that A remained constant, notwithstanding large changes in the value of B due to changes of configuration, of these remaining active carbons. This would certainly indicate that in all of these cases, some 30 or more, the activity of the A carbon was changed neither in value nor sign, by configuration changes in the balance of the molecule.[2]

In most of these cases the agreement was well within the limits of experimental error.

These investigations clearly indicate the establishment of Hudson's original proposition, that in the case of a pair of multirotating sugars, reaching an equilibrium in solution, the rotations, either molecular or specific, are the algebraic sum of two constants A and B so that $[\alpha]_D = B \pm A$ where A is a constant corresponding to the end asymmetric carbon, its sign depending upon the configuration of the A carbon and B is the joint effect of all of the remaining asymmetric atoms in the molecule.

Changes in the value of B, caused by changes of configuration of the α, β, γ, δ, etc., carbons, do not change the constant difference of 2A, and so do not affect the activity of the A carbon in either magnitude or sign. This principle of Hudson's has been universally accepted, and is held by such workers as Dr. Levene of the Rockefeller Institute of Medical Research[3] to afford "telling evidence in support of the principle of optical superposition." It should be further noted that Hudson's work establishes the principle for other carbons than the end carbon A. Thus for instance the 2

[1] THIS JOURNAL, 31, 69 (1909).

[2] For the use of those interested the following references to some of this work are given below: THIS JOURNAL, 31, 69 (1909), glucose, galactose, arabinose and lactose; *Ibid.*, 36, 1265 (1914), glucosepentacetate and tetracetyl, methylglucoside; *Ibid.*, 37, 1275 (1915), xylosetetracetate, glucosepentacetate and lactose octacetate; *Ibid.*, 37, 1276 (1915), maltose, cellose and lactose octacetates; *Ibid.*, 38, 1434 (1916), glucosamine and chondrosamine pentacetates; *Ibid.*, 38, 1576 (1916), hexacetylglucoheptose, glucosepentacetate, and maltose pentacetate; *Ibid.*, 39, 1035 (1917), thirteen miscellaneous aldose sugars; *J. Ind. Eng. Chem.*, 8, 379 (1906), monomethylglucose and glycol glucosides.

[3] *J. Biol. Chem.*, 23, 145 (1915).

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sugars α,δ-glucose and α,δ-galactose differ only in the configuration of the γ carbon, the difference of their specific rotations being $+113.4° - 144° = -30.6$ as the value of 2 γ. If now we change the configuration of the A carbon of these 2 sugars by reversing the positions of H and OH we have the β forms of both sugars thereby produced, but the difference between β,δ-glucose and β,δ-galactose remains practically unchanged being $+19° - 52° = -33°$ for 2 γ against $-30.6°$ for 2γ as previously obtained, showing that changing the configuration of the A carbon has no affect upon either the magnitude or sign of the constant of the γ carbon.

Summary.

It has been shown, not only for the 4 metasaccharins but also for their strychnine, brucine and quinine salts:

First, that their specific and molecular rotations are in each case the algebraic sums of three constants corresponding to the 3 active atoms present, the signs of the constants being taken + or — with H to the right or left in vertically written formulas with the A carbon below thus proving the validity of the principle of optical superposition in these cases.

Second, that the constants are practically identical for the α carbon in the three classes of salts, and likewise for the γ carbon, but differ considerably from the α and γ constants for the saccharins themselves, which was to have been expected in view of the fact that ring structure is present in the saccharins, and chain structure in their salts.

Third, the sum of the activities of the δ carbon and the active base, remains constant for the 4 salts of each of the 3 bases, but changes its value with change of base.

Fourth, by using the average value of the molecular α and γ rotation constants for the three sets of salts, in connection with the sum of the molecular constants of the base and of the δ carbon, the specific rotations of the 12 salts have been computed, with an average departure from observed values of less than 0.5°, the average errors being as follows, *viz.*, 0.94° for the strychnine salts, 0.25° for the brucine salts, and 0.22° for the quinine salts, the algebraic sum of the departures for the entire series of 12 compulations being only 0.16°.

Fifth, the work of Dr. Hudson and his co-workers has been briefly tabulated, showing conclusively that in 30 different instances, the activity of the A carbon is not greatly changed by configuration changes in other parts of the molecule and proving that Van't Hoff's principle applies to the A carbon in many of the sugars and their derivatives.

Sixth, it has also been pointed out that this work of Dr. Hudson likewise proves that the activities of other carbons, *e. g.*, the γ carbon are unaffected by configuration changes on the A carbon, and that Van't Hoff's principle is therefore valid for carbons other than the A or terminal carbon.

WASHINGTON, D. C.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF RUTGERS COLLEGE.]

THE ACTION OF THIONYL AND SULFURYL CHLORIDES ON SULFUR AND PHOSPHORUS.

BY H. B. NORTH AND J. CLAUDE THOMSON.

Received February 21, 1918.

In 1882 Köchlin and Heumann[1] described an investigation of the action of sulfuryl chloride on several substances, among which were sulfur and phosphorus. Inasmuch as the experiments described were carried on under ordinary atmospheric pressure, the temperature could not have been higher than 69°, the boiling point of the reagent. According to Köchlin and Heumann, sulfuryl chloride reacts only slowly with yellow phosphorus, but with well-dried red phosphorus the reaction proceeds readily even at the ordinary temperature, with the formation of phosphorus trichloride. This compound was separated from the excess of sulfuryl chloride by fractional distillation. Reaction proceeds according to the equation

$$2P + 3SO_2Cl_2 = 2PCl_3 + 3SO_2.$$

The failure of yellow phosphorus to react was considered to be due to the limited surface of contact. Sulfuryl chloride was found by Köchlin and Heumann to be without action on sulfur at the boiling point of the former.

The action of thionyl chloride on sulfur was described by Prinz[2] in 1884. The experiments were carried out in sealed glass tubes. At 100° the sulfur was found to dissolve to form a clear solution but upon cooling it separated in the form of crystals. After heating the tubes for a time at 180°, the sulfur was found to have reacted according to the equation

$$2SOCl_2 + 3S = 2S_2Cl_2 + SO_2.$$

So far as the authors of this article are able to find, no attempts have been made to bring about reaction between thionyl chloride and phosphorus either red or yellow.

The experiments described in this paper were carried out in sealed glass tubes at temperatures varying from 70° to 180°. The sulfur flowers and red phosphorus were carefully dried over sulfuric acid; the yellow phosphorus was dried on filter paper. Except where otherwise stated, an excess of the reagent was employed.

Sulfuryl Chloride and Sulfur.—Tubes containing sulfuryl chloride and sulfur were heated at temperatures varying between 75° and 150°. At temperatures from 75° to 85°, the sulfur was found to dissolve in the liquid and to crystallize out upon cooling. Upon opening the tubes no indication of chemical reaction was noted. At 95° to 98° reaction was found to take place slowly for upon cooling tubes which had been heated at these temperatures for several hours, only about one-fifth of the sulfur separated out.

[1] *Ber.*, **15**, 1736 (1882).

[2] *Ann.*, **223**, 355 (1884).

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At temperatures of 125° and above, all the sulfur went into solution within 2 hours but did not crystallize out when the tubes were cooled. Reaction apparently was complete. The color of the solution in these tubes varied from light yellow to dark amber, depending upon the relative amounts of sulfur and sulfuryl chloride employed. A rough fractional distillation of the solution led to the identification of sulfur monochloride and the excess of sulfuryl chloride. Sulfur dioxide was likewise present to considerable extent. Reaction evidently proceeds according to the equation

$$SO_2Cl_2 + 2S = S_2Cl_2 + SO_2.$$

Sulfuryl Chloride and Phosphorus.—As previously mentioned this reaction was investigated by Köchlin and Heumann who found the product of the reaction to be phosphorus trichloride. Inasmuch as sulfuryl chloride is a good oxidizing agent, the authors of this paper considered that the reaction with excess of sulfuryl chloride should proceed further and that the ultimate product formed should be phosphorus pentachloride. Accordingly a number of tubes were prepared with red phosphorus and an excess of the reagent. After the tubes were heated for a time at 120°, the phosphorus was found to have gone entirely into solution with the formation of phosphorus trichloride, as described by Köchlin and Heumann. Higher temperatures were then tried. At 180° reaction proceeds further, for after heating for a time at this temperature the tubes were found to contain a small amount of a light yellow crystalline deposit which proved to be phosphorus pentachloride. The supernatant liquid contained the greater part of the phosphorus in the form of trichloride. From this it is seen that phosphorus trichloride is oxidized to phosphorus pentachloride by excess of sulfuryl chloride, but that reaction is far from complete at 180°. Equations for the action of sulfuryl chloride on phosphorus are as follows:

$$3SO_2Cl_2 + 2P = 2PCl_3 + 3SO_2$$

$$PCl_3 + SO_2Cl_2 = PCl_5 + SO_2$$

The complete reaction of an excess of sulfuryl chloride on phosphorus may be expressed in a single equation as follows:

$$2P + 5SO_2Cl_2 = 2PCl_5 + 5SO_2$$

After completing the above experiments with red phosphorus, other tubes were prepared using yellow phosphorus. Reaction was found to take place readily at a temperature of 125° with formation of phosphorus trichloride according to the equation given above for red phosphorus. As stated heretofore, Köchlin and Heumann found that sulfuryl chloride and yellow phosphorus react very slowly. This difference in results is undoubtedly due to the fact that Köchlin and Heumann carried on their experiments under ordinary pressure, hence at a temperature not exceeding 69°, whereas the authors of the present paper employed a temperature of 125°.

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Thionyl Chloride and Sulfur.—The reaction of thionyl chloride on sulfur was described by Prinz as previously mentioned. This work has been repeated by the authors with precisely the same results as those described by Prinz. At temperatures from 150° to 180°, reaction takes place giving sulfur dioxide and sulfur monochloride.

Thionyl Chloride and Phosphorus.—Although this reaction has never been investigated, the action of thionyl chloride on phosphorus trichloride was described by Michaelis[1] in 1871. According to Michaelis, when phosphorus trichloride and thionyl chloride are heated together in the proportion of 3 molecules of the former to one of the latter, reaction takes place with the formation of phosphorus pentachloride, phosphorus oxychloride and phosphorus sulfochloride, as shown by the equation

$$3PCl_3 + SOCl_2 = PCl_5 + POCl_3 + PSCl_3.$$

Reaction however, is not complete even after heating for 15 or 20 hours.

This reaction differs greatly from the thionyl chloride reactions heretofore studied by the authors, hence the work has been repeated, tubes being prepared with phosphorus trichloride and thionyl chloride in the proportions employed by Michaelis. These tubes were heated for 16 hours at temperatures from 80° to 160°, after which they were found to contain a yellowish crystalline substance together with the supernatant liquid. The solid proved to be phosphorus pentachloride. On account of the small amount, it was impossible to fractionate the supernatant liquid with any degree of completeness. Nevertheless a rough fractionation yielded a small quantity having a boiling point above 110°. When this was decomposed in water, considerable hydrogen sulfide was liberated, undoubtedly due to phosphorus sulfochloride which is decomposed by water according to the equation

$$PSCl_3 + 4H_2O = H_3PO_4 + 3HCl + H_2S.$$

It has been impossible to identify positively the phosphorus oxychloride but the lower boiling portion of the liquid was found to contain both thionyl chloride and phosphorus trichloride. From this it appears that the reaction as described by Michaelis is correct but incomplete at the temperature employed.

Several tubes were prepared with the element phosphorus and a considerable excess of thionyl chloride. After heating for 2 hours at 125°, the phosphorus was found to have gone completely into solution. This was true with both the yellow and red varieties of the element. Reaction proceeds according to the equation

$$2P + 4SOCl_2 = 2PCl_3 + 2SO_2 + S_2Cl_2.$$

Other tubes were heated for several hours at a temperature close to 180°. These were found upon cooling to contain small amounts of phosphorus

[1] *Z. Chem. Ph. Math.*, 7, 151 (1871); abstract, *Bull. soc. chim.*, [2] 15, 185 (1871).

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pentachloride. Sulfur dioxide was evolved to a slight extent when the tubes were opened. The supernatant liquid consisted chiefly of the excess of thionyl chloride and phosphorus trichloride, but in addition sulfur monochloride also was detected. It was thought that the oxidizing action of the excess of thionyl chloride on the phosphorus trichloride had proceeded according to the equation

$$3PCl_3 + 4SOCl_2 = 3PCl_5 + 2SO_2 + S_2Cl_2,$$

which is quite different from that given by Michaelis. However, it is certain that reaction does not follow the above equation quantitatively, inasmuch as in every case decomposition of the liquid contents of the tubes by means of water gave appreciable quantities of hydrogen sulfide, indicating that to some extent at least, reaction follows the equation given by Michaelis.

Summary.

Thionyl and sulfuryl chlorides react with sulfur at temperatures from 150° to 180° with formation of sulfur dioxide and sulfur monochloride. Under similar conditions both reagents react with phosphorus, either red or yellow, with the formation of phosphorus trichloride. Prolonged heating tends to cause the trichloride to become pentachloride, but the reaction is far from complete even after heating for several hours at 160° to 180°.

New Brunswick, N. J.

[Contributions from the Department of Chemistry, Throop College of Technology, No. 4.]

THE USE OF METALLIC SILVER AS A REDUCING AGENT IN THE VOLUMETRIC ESTIMATION OF IRON.

By Graham Edgar and A. R. Kemp.

Received March 16, 1918.

I. Purpose of the Investigation.

Several investigators have studied the reaction between metallic silver and solutions of ferric salts, and have shown that it proceeds to an equilibrium, in which at room temperature a considerable concentration of ferric salt is usually present. This fact apparently renders silver unsuitable as a reducing agent for the quantitative estimation of iron. However, if the silver-ion concentration in the solution is reduced (*e. g.*, by precipitation) the equilibrium may be shifted until only inappreciable quantities of ferric iron remain in the solution. Thus Hoenig[1] has shown that in the presence of a sufficient concentration of hydrochloric acid, ferric chloride may be reduced to the ferrous state by metallic silver with sufficient completeness to permit the quantitative estimation of the iron by titration with potassium permanganate after filtering off the silver chloride and the excess of silver.

[1] *Z. anal. Chem.*, 54, 441 (1915).

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In the present investigation the reaction between metallic silver and solutions of ferric sulfate in the presence of sulfuric acid and a soluble thiocyanate has been studied. The results show that the reduction of the ferric iron is sufficiently complete for the purposes of quantitative analysis, and that the reaction may serve as the basis of a procedure for the estimation of iron which is rapid and accurate, and which possesses certain other advantages over many standard procedures.

II. Experimental.

Materials.—The silver used in these experiments was in some cases prepared electrolytically by a method previously described[1] and in other cases by reduction of ammoniacal silver nitrate solution by tartaric acid or cuprous chloride. It was in all cases given a preliminary purification by boiling it with dilute sulfuric acid, filtering, and washing it thoroughly.

The solutions of ferric sulfate and potassium permanganate were carefully standardized, and proper precautions of measurement, such as the use of calibrated burets, and correction of end points, were observed throughout.

Technique and Results. Procedure 1.—After a series of preliminary experiments a number of quantitative determinations were carried out as follows: A measured volume of standard ferric sulfate solution, containing 0.05 to 0.20 g. iron, was acidified with 3 cc. conc. sulfuric acid (sp. gr. 1.84), diluted to about 75 cc., and treated with about 3 g. metallic silver. The mixture was heated to boiling in a small flask and boiled gently until the solution became nearly colorless (usually one or two minutes). To the boiling solution was then added, drop by drop, sufficient ammonium thiocyanate solution (about 0.5 *N*) to precipitate all of the silver dissolved in the reaction and give a small excess.[2] The solution was then boiled gently until it became perfectly colorless (usually not more than a minute or two), cooled under the tap or allowed to stand until cool, filtered, and the residue washed thoroughly with cold water. To the filtrate was added a little ferric sulfate solution and then enough dilute silver nitrate solution to discharge the red color of ferric thiocyanate. The mixture was then titrated with 0.1 *N* potassium permanganate solution, without filtering off the

[1] Edgar, This Journal, 38, 1297 (1916).

[2] With moderate quantities of iron (0.1 to 0.2 g.) the presence of an excess of ammonium thiocyanate is usually indicated by the appearance of a faint red color of ferric thiocyanate, persisting through the solution for a short time. With smaller quantities of iron the equilibrium shifts so rapidly, as the silver ion is precipitated by the ammonium thiocyanate, that this color is not always apparent. If there is any doubt as to the presence of an excess of ammonium thiocyanate a small drop of the solution may be removed on the end of a glass rod and tested with ferric chloride solution. A considerable excess of ammonium thiocyanate may be added without interfering with the accuracy of the determination, but it is undesirable, since this excess must be precipitated later by silver nitrate.

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silver thiocyanate, to the first persistent faint pink color. The results are given in Table I. They will be discussed below.

TABLE I.

Fe taken. Gram.	0.1 *N* $KMnO_4$. Cc.	Fe found. Gram.	Error. Gram Fe.
0.0526	9.42	0.0526	0.0000
0.0548	9.86	0.0550	0.0002
0.0688	12.32	0.0688	0.0000
0.1381	24.73	0.1381	0.0000
0.1381	24.74	0.1381	0.0000
0.1385	24.76	0.1383	0.0002
0.1243	22.27	0.1244	0.0001
0.1243	22.28	0.1244	0.0001
0.1317	23.54	0.1314	0.0003
0.1317	23.60	0.1318	0.0001
0.1976	35.40	0.1977	0.0001
0.1976	35.35	0.1974	0.0002
0.1976	35.35	0.1974	0.0002
0.1317[1]	23.60	0.1318	0.0001
0.1317[2]	23.60	0.1318	0.0001
0.1263[3]	22.63	0.1263	0.0000

The above experiments were selected purely at random from about three times the number of similar determinations.

Procedure 2.—A second series of determinations was made by a different method. A measured portion of ferric sulfate solution was acidified with about 3 cc. concentrated sulfuric acid, diluted to a volume of about 75 cc., and treated with 3 to 5 g. silver and with ammonium thiocyanate solution in excess of that necessary to precipitate the silver dissolved in the reaction. The dark red solution was then shaken in the cold until it became perfectly colorless (usually 3 to 12 minutes). It was then filtered, and the filtrates treated with silver nitrate and titrated with potassium

TABLE II.

Expt. No.	Fe taken. Gram.	0.1 *N* $KMnO_4$. Cc.	Fe found. Gram.	Error. Gram Fe.
1[4].....	0.0658	11.80	0.0658	0.0000
2[4].....	0.1317	23.61	0.1318	0.0001
3[4].....	0.1976	35.39	0.1977	0.0001
4[4].....	0.1976	35.37	0.1976	0.0000
5[5].....	0.0658	11.77	0.0657	0.0001
6[5].....	0.1263	22.64	0.1264	0.0001
7[5].....	0.1263	22.63	0.1263	0.0000
8[5].....	0.1976	35.36	0.1975	0.0001
9[5].....	0.1317	23.60	0.1318	0.0001

[1] 5 cc. H_2SO_4 (sp. gr. 1.8) added.
[2] 10 cc. H_2SO_4 (sp. gr. 1.8) added.
[3] Ag spiral made from Ag wire was used. Time, 30 min.
[4] 3–5 g. Ag used. Shaken in cold. Time of reaction 3–12 min.
[5] 3–5 g. Ag used. Heated on water bath and shaken. Time 3–12 min.

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permanganate as in the first procedure. The results of these experiments are given in Table II. In a few of the experiments the procedure was varied somewhat, and where this was done a note describes the changes made.

Procedure 3.—Since silver does not dissolve in the dil. sulfuric acid except by virtue of its reaction with the ferric salt, the amount dissolving should be a measure of the ferric salt present, and it should be possible to estimate the ferric salt by determining this dissolved silver. To ascertain whether or not this was feasible a number of determinations were made by Procedures 1 and 2, except that the ammonium thiocyanate and silver nitrate solutions were carefully standardized and carefully measured, and at the conclusion of the potassium permanganate titration[1] the excess of silver nitrate in the solution was determined by titration with standard ammonium thiocyanate, using ferric sulfate as indicator. From the total amounts of ammonium thiocyanate and silver nitrate solutions used, the silver dissolved in the reaction (and from it the ferric iron present) was calculated. The results obtained by this procedure were invariably slightly high when the reduction was carried out in boiling solution (as in Procedure 1), and these results are not tabulated. Where reduction was carried out in the cold (as in Procedure 2), results were obtained which agreed closely with the potassium permanganate titration, and with the true values. These results are given in Table III.

TABLE III.

Expt. No.	Fe taken. Gram.	0.1 *N* $KMnO_4$. Cc.	Fe found by $KMnO_4$. Gram.	0.1 *N* NH_4CSN.[2] Cc.	Fe found by NH_4CSN. Gram.
1.....	0.1317	23.58	0.1317	23.57	0.1316
2.....	0.1317	23.62	0.1319	23.62	0.1319
3.....	0.1317	23.58	0.1317	23.55	0.1315
4.....	0.1263	22.60	0.1262	22.62	0.1264
5.....	0.1263	22.63	0.1263	22.63	0.1263

All shaken in the cold with 3 g. Ag. Time 8–10 min.

Test Analyses of Iron Ores.—To test the applicability of these procedures to the analysis of iron ores determinations were carried out upon the Bureau of Standards' "Crescent Iron Ore," No. 26, and upon their "Sibley Iron Ore," No. 27. Weighed samples of the ores were treated with hydrochloric acid, filtered from the insoluble residue, the filtrate treated with 5 cc. of conc. sulfuric acid, evaporated to the fuming point and heated until all hydrochloric acid was expelled. The insoluble residue was decomposed with hydrofluoric acid and sulfuric acid and the solution added to the main portion. The resulting solution was then diluted to 75 cc., treated with 3 to 5 g. of silver, and analyzed according to the directions given above,

[1] In an actual analysis the potassium permanganate titration may, of course, be omitted.

[2] After subtracting the cc. 0.1 *N* $AgNO_3$ used.

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Procedure 1 being used in the case of the "Crescent" ore, and Procedure 2 in the case of the "Sibley" ore. The results are given in Table IV.

TABLE IV.

Sample, gram.	0.1 N $KMnO_4$, cc.	% Fe in sample.	B. of S. value.
"Crescent Iron Ore," B. of S. Sample No. 26.			
0.2019	21.19	58.59	...
0.3097	32.52	58.64	...
0.3039	31.85	58.52	...
	Average,	58.58	58.62
"Sibley Iron Ore," B. of S. Sample No. 27.			
0.3500	43.40	69.25	...
0.3526	43.73	69.25	...
0.3570	44.25*	69.22	...
0.3597	44.60*	69.24	...
	Average,	69.24	69.26

III. Discussion.

The results tabulated in Tables I, II, III, and IV, together with numerous other experiments not here recorded, lead to the following conclusions:

1—Metallic silver may be used to effect the complete reduction of ferric sulfate to ferrous sulfate, provided the silver dissolved in the reaction is precipitated by a thiocyanate. The resulting ferrous solution may be titrated with potassium permanganate, after filtering off the silver and then precipitating the excess of thiocyanate with silver nitrate solution. The titration measures very accurately the amount of iron present.

2—Three separate procedures may be employed by which iron may be estimated by means of the reaction. In Procedure 1 the ferric sulfate solution is heated at first with the silver alone, and the thiocyanate solution is added after a considerable portion of the iron is reduced. In Procedure 2 the reduction is carried out in the cold, and the thiocyanate is added at the beginning of the reaction. Procedure 3 differs from Procedure 2 only in the use of standard thiocyanate and silver nitrate solutions, which permits the estimation of the iron by means of these solutions instead of by potassium permanganate.

3—The time required for the estimation of iron by Procedure 1 is very short. The reduction is complete in 2 or 3 minutes, and the solution may be cooled, filtered and titrated in 5 to 10 minutes more. The reduction proceeds somewhat more slowly in the cold (Procedure 2), but even in this case it is usually complete in 4 to 12 minutes, which compares very favorably with the time required by almost any other standard method of

* In these two determinations the residues of Ag and AgCNS were not thoroughly washed, and it was found that on further washing an amount of Fe was obtained which required 0.05 cc. of $KMnO_4$ to reoxidize it. This correction was applied in the results given above.

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analysis. This is especially true when a considerable number of determinations are to be carried out at once.

4—Procedure 3 makes it possible to check the potassium permanganate titration by also estimating the silver dissolved in the reduction, or to determine iron by means of standard silver nitrate and ammonium thiocyanate alone. It may also serve, if desired, for the analysis of a solution containing both ferrous and ferric salts; for the results of the ammonium thiocyanate titration give the ferric iron present, while the potassium permanganate titration gives the total iron.

5—A distinct advantage of these methods over practically every other method for the reduction of ferric iron is that there is never any uncertainty as to whether the reduction is complete. The thiocyanate serves as a very sensitive indicator, and the disappearance of the red color of ferric thiocyanate gives an absolute indication that no ferric salt remains.

6—The reduced solution may be left in contact with the silver, without the slightest danger of reoxidation by the air for as long as 24 hours or more; for any ferric iron formed by atmospheric oxidation is at once reduced by the silver. This is especially advantageous where several determinations are being made at once, as there need be no hurry about filtering the solutions.

7—The statement is sometimes made that ferrous solutions even when cold, can not be filtered without undergoing appreciable oxidation. That this is incorrect is shown by the fact that the solutions in the above experiments, containing an excess of thiocyanate, remained perfectly colorless during the filtration, and for some time thereafter.

8—The presence of the precipitate of silver thiocyanate during the potassium permanganate titration does not influence the result, provided the solution is cold and the potassium permanganate is added at a reasonable rate. The pink color at the end point may fade out upon standing somewhat more rapidly than is the case with iron solutions alone; but there is not the slightest difficulty in obtaining a perfectly sharp end point. If the solution is warm, the potassium permanganate may act appreciably upon the silver thiocyanate and introduce error.

9—The accuracy of the results is practically independent of the amount of silver taken, its method of preparation, the amount of sulfuric acid used, and the excess of ammonium thiocyanate added, within rather wide limits. Thus the amount of silver was varied between 2 and 5 g., the sulfuric acid between 1 and 10 cc. of conc. acid in a volume of 75 cc., and in some cases nearly twice the necessary amount of ammonium thiocyanate was added, without any apparent effect upon the accuracy of the determination. The speed of the reaction, however, varies somewhat with the amount of silver added and its state of subdivision, the concentration of ferric sulfate, and the particular technique used. The directions given in

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the three procedures give perhaps the most convenient and satisfactory quantities of material and methods of operation; but they may be varied considerably, if desired.

10—A number of experiments were made to determine the effect of foreign substances upon the reaction. These experiments showed that hydrochloric acid in more than small amounts is apt to be acted upon by the permanganate under the conditions of the determination, and thus introduce error; nitric acid in small amount does not usually affect the determination unless Procedure 3 is being employed; it is best, however, to remove both of these acids by evaporation with sulfuric acid and heating. Molybdic acid is irregularly reduced and thus introduces error. Chromic acid is completely reduced, but if present in appreciable amount it uses up some permanganate. Vanadic acid is quantitatively reduced to the quadrivalent state, and may be corrected for. Titanium is not reduced at all.

11—Comparing briefly silver as a reducing agent for ferric sulfate with some other substances commonly employed, we may note the following facts: (*a*) Silver is readily obtained perfectly free from iron, which is never the case with zinc or aluminum. This renders blank determinations unnecessary. (*b*) It reduces vanadic acid definitely to the quadrivalent state, and does not reduce titanium at all, whereas zinc and aluminum reduce vanadic acid irregularly, and also reduce titanium. (*c*) It is much more rapid in its action and more certain in its results than such substances as sulfur dioxide and hydrogen sulfide. (*d*) By the use of the thiocyanate solution not only is the reaction brought to completion, but the point of complete reduction is sharply indicated by the color of the solution—an advantage over every other standard method.

12—Although metallic silver is somewhat expensive, it may be readily recovered from the residues of silver and silver thiocyanate by treatment with ammonium hydroxide and tartaric acid or cuprous chloride, and thus prepared for use again with very little trouble.

IV. Summary.

In this article has been described a new process for the volumetric estimation of iron, based upon the fact that ferric sulfate is reduced to ferrous sulfate by metallic silver in the presence of a thiocyanate. The reduced solution after filtration is treated with an excess of silver nitrate, and the ferrous iron is titrated with potassium permanganate (or if preferred the excess of silver nitrate may be titrated back with thiocyanate). Test analyses with known ferric sulfate solutions and with samples of iron ores standardized by the Bureau of Standards are presented which show that the method is one of high accuracy. The method has the advantages (1) that the thiocyanate serves to show when the ferric iron is completely reduced; (2) that silver, unlike zinc and aluminum, is ordinarily entirely

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free from iron, making blank determinations unnecessary; and (3) that silver does not reduce titanium at all, and reduces vanadium definitely to the quadrivalent state. The method is rapid in execution.

PASADENA, CAL.

NOTE.

Grinding Glass Tips for Drop-Weight Apparatus.—In order to make glass tips for use in "drop-weight" surface-tension measurements the usual procedure is to first grind the glass in a precision lathe until the cross section of the tube near the tip is a circle. This lateral surface is polished until it is smooth. It is then necessary to grind down the end of the tube until it is flat and the edges are sharp. In order to avoid chipping during the process various devices have been used. One of the most efficient of these methods previously used is that of imbedding the tip in a brass disc which is perfectly flat on the bottom. The hole through the brass is just a little larger than the glass tube. The latter is held in place by special wax which is melted, poured around the tube and allowed to harden. Glass tip and brass are then ground away simultaneously. However considerable trouble is experienced because particles of abrasive work into the wax around the edge of the tip. Fine glass and abrasive likewise work up into the small capillary opening and frequently become so tightly wedged into it that it is not possible to dislodge them without injury to the tip. When no supporting device is used for the tip while grinding the flat surface, lead glass is sometimes used because it is less easily splintered. However this kind of glass is often objectionable where it is necessary to seal the tip to another glass tube, as when an interface apparatus is to be made. It is also often desirable to use a glass which is not so easily attacked by strong reagents. Moreover, when viewed under the microscope a tip ground without having been inbedded in some supporting material not infrequently shows an imperfect edge.

To get around the use of the wax and in order to have a firm support for the tip edge during the grinding of the flat surface, the author has found Wood's metal or other similar low melting alloy to be admirable. Wood's metal melts at 65.5°; so that the glass will not be much heated by the molten alloy. The glass tube made ready for the final preparation of the face of the tip is supported in a vertical position with the tip against the flat bottom of a small cardboard box. The Wood's metal is melted in a test tube in a water bath and poured around the tip to a depth of about 10–15 mm. By raising and lowering the tube in the molten alloy or by applying a little suction to the tube the alloy is drawn a short distance into the capillary opening. Finally the tube is left with the tip against the bottom of the box until the alloy has solidified. When the paper is removed it is found that the tip is firmly imbedded in the alloy. Tube

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and alloy are then ground with about No. 180 carborundum on a flat, hard surface until the desired sharp edge is obtained.

To remove the Wood's metal from the tube and the small capillary opening it is only necessary to put the tip end into a test tube immersed in boiling water and allow the alloy to melt. The latter is then ready for another tube.

The effective radius of the glass tip is generally determined by getting the average weight of drops of water given at a definite temperature. Hence it is quite possible by a proper selection of a capillary tube with suitable size of wall and comparatively circular cross section to omit the previous grinding of the lateral surface. This gives a tip with a sharp edge and the glazed wall makes creeping impossible. Such tips can certainly be substituted for the more expensive ones where only a fair degree of accuracy is wanted and where a considerable outlay of money or waste of time would be involved in getting a proper assortment of sizes.

The method of grinding just outlined is especially useful when it becomes necessary to regrind a much-needed tip whose face has become slightly chipped.

EARL C. H. DAVIES.

BUSCH HALL, WASHINGTON UNIVERSITY,
ST. LOUIS, MO.

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY OF THE MICHIGAN AGRICULTURAL COLLEGE.]

ACTION OF AROMATIC ALCOHOLS ON AROMATIC COMPOUNDS IN THE PRESENCE OF ALUMINUM CHLORIDE. II.

SECONDARY ALCOHOLS.

BY RALPH C. HUSTON AND THEODORE E. FRIEDEMANN.

Received January 31, 1918.

The first article of this series[1] dealt with the condensation of a primary aromatic alcohol, benzyl alcohol, with benzene, using anhydrous aluminum chloride as a dehydrating agent.

In the present paper experiments are described in which some secondary alcohols were allowed to react with benzene under the influence of the same dehydrating agent. Three alcohols were studied. Two of these, methylphenylcarbinol and ethylphenylcarbinol, may be regarded as mixed aromatic aliphatic alcohols. The third, diphenylcarbinol or benzhydrol, is a true secondary aromatic alcohol. A comparative study of these three compounds should, therefore, give us some idea as to the relative effects of aryl and alkyl groups upon the reaction at hand.

It has been shown in the first article that the principal product of the reaction between benzyl alcohol and benzene in the presence of aluminum chloride is diphenylmethane.

[1] THIS JOURNAL, 38, 2527 (1916).

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$$C_6H_5CH_2OH + C_6H_6 \xrightarrow{AlCl_3} C_6H_5CH_2C_6H_5 + H_2O.$$

If equimolecular amounts of the reacting substances are used, the yield of diphenylmethane is not large (about 30%) and the yields of secondary products (*p*- and *o*-dibenzylbenzene, anthracene and tar) are quite large. If, however, an excess (5 mols) of benzene is used the yield of diphenylmethane is greatly increased, while the yields of secondary products are correspondingly decreased.

A rather large number of experiments was made with methylphenyl carbinol, benzene and aluminum chloride, in which the relative amounts of the reacting substances were varied over a wide range. In each case there was formed a considerable amount of 1,1-diphenylethane, as represented by the following equation:

$$C_6H_5CHOHCH_3 + C_6H_6 \xrightarrow{AlCl_3} (C_6H_5)_2CHCH_3 + H_2O$$

If equimolecular amounts of the reagents were used and the aluminum chloride was added in such quantities that the temperature was kept between 25° and 35° the yield of 1,1-diphenylethane was small (about 20%) and secondary products were formed in large amounts. These last consisted of ethylbenzene, diphenylmethane, anthracene and a tarry residue from which we were unable to isolate fractions of constant boiling point.

Since aluminum chloride has the property of eliminating phenyl groups from substituted methane derivatives,[1] we believe that we are justified in the assumption that the ethyl benzene was formed as a result of the elimination of a phenyl group from 1,1-diphenylethane under the influence of aluminum chloride.

The yield of diphenylmethane was small and its separation from 1,1-diphenylethane was very difficult. We were able, however, after more than 25 distillations, to obtain a small amount of the compound which was identified by its boiling point and oxidation to benzophenone. It was probably formed by the elimination of the methyl group of 1,1-diphenylethane, under the influence of aluminum chloride.

Anthracene is a product of the reaction between diphenylmethane and aluminum chloride. Its formation in this reaction was probably preceded by the formation of diphenylmethane. Methylphenylcarbinol or 1,1-diphenylethane would be expected to yield a homolog of anthracene and not anthracene itself.[2]

An experiment in which one molecular equivalent of methylphenylcarbinol was allowed to react with 5 molecular equivalents of benzene and 0.5 molecular equivalent of aluminum chloride, and in which the temperature was kept below 40°, gave a larger yield of 1,1-diphenylethane

[1] Silva, *Bull. soc. chim.*, [2] **41**, 448 (1884); Auger, *Ibid.*, [2] **47**, 49 (1887); Meyer and Jacobson, "Lehrbuch der Organischen Chemie," **3**, 113; etc.

[2] Radziewanowski, *Ber.*, **27**, 3238 (1894); Anschutz, *Ann.*, **235**, 305 (1886).

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(about 30%), a small amount of ethylbenzene (about 10%), only a trace of anthracene and a small amount of tarry residue.

The best yields of 1,1-diphenylethane were obtained by keeping the temperature below 10° and using one-half of a molecular equivalent of aluminum chloride to one molecular equivalent of methylphenylcarbinol and 5 of benzene. In these experiments from 8 to 10% of the alcohol was recovered unchanged and the yield of 1,1-diphenylethane was almost 65%. Only about 4 to 5% of the theoretical amount of ethylbenzene was isolated. We were not able to isolate diphenylmethane or anthracene. The amount of residual tar was quite small.

In all of the experiments with ethylphenylcarbinol, benzene and aluminum chloride, an excess (5 mols) of benzene was used, the temperature and amounts of aluminum chloride being varied.

When one molecular equivalent of ethylphenylcarbinol was mixed with benzene in excess and one molecular equivalent of aluminum chloride was added in such quantities that the temperature was between 35° and 40°, 10 to 12 % of the alcohol was recovered unchanged. A yield of 23 to 25% of 1,1-diphenylpropane was obtained.

$$C_2H_5CHOHC_6H_5 + C_6H_6 \xrightarrow{AlCl_3} C_2H_5CH(C_6H_5)_2 + H_2O.$$

Propylbenzene was formed to the extent of about 14% of the theory by the elimination of a phenyl group from the 1,1-diphenylpropane. Diphenylmethane was formed to the extent of about 7% by the elimination of the ethyl group. Anthracene was isolated from the high boiling fraction equal in weight to about 5% of the weight of the ethylphenylcarbinol decomposed.

When the experimental conditions were the same as those just described except that the amount of aluminum chloride was reduced to a little more than 0.5 molecular equivalent and the temperature was kept below 10°, about 15% of the alcohol was recovered unchanged. The yield of 1,1-diphenylpropane was increased to about 40% of the theory. The propylbenzene amounted to about 12% and the diphenylmethane to about 4% of the theory. No evidence of the formation of anthracene was found under these conditions. If the temperature of the reacting mixture was allowed to rise to 40° the yield of 1,1-diphenylpropane was decreased while the yields of propylbenzene, diphenylmethane and tarry residue were correspondingly increased.

The condensation of benzhydrol with benzene under the influence of aluminum chloride takes place more rapidly and completely than does the condensation of either methylphenylcarbinol or ethylphenylcarbinol. One molecular equivalent of benzhydrol, 5 of benzene and one of aluminum chloride react at 35–40° to give a yield of about 40% of triphenylmethane:

$$(C_6H_5)_2CHOH + C_6H_6 \xrightarrow{AlCl_3} (C_6H_5)_3CH + H_2O$$

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together with about 15% of the theoretical amount of diphenylmethane. If the aluminum chloride was added in smaller portions while the temperature was kept below 10° by cooling in ice, the yield of triphenylmethane was increased to between 65 and 70% and the amount of diphenylmethane formed was very small (about 1%).[1]

The Friedel and Crafts method for preparing triphenylmethane from chloroform benzene and aluminum chloride[2] is open to the objection that the heating of the reaction mixture brings about the formation of considerable amounts of diphenylmethane and tarry residue. By the use of benzhydrol, benzene and aluminum chloride at low temperatures, there is practically no diphenylmethane formed and the tarry residue is very small. The product is practically pure after one crystallization from alcohol.

From the experimental evidence here presented we may conclude that methyl and ethyl groups interfere to some extent with the condensation of aromatic alcohols with benzene and that the ethyl group has a greater retarding effect than the methyl group. The presence of a second phenyl group in the carbinol molecule on the other hand does not seem to interfere in any way with the condensation. It would rather appear that benzhydrol condenses with benzene more readily than does benzyl alcohol.

Secondary alcohols of the type used in these reactions are very easily prepared from aromatic aldehydes and alkyl or aryl halides by the Grignard synthesis. The method should, therefore, be valuable as a general method for the preparation of derivatives of diphenylmethane and triphenyl methane.

Work in this field is being continued.

Experimental.

Materials.—Methylphenylcarbinol was prepared from benzaldehyde and methyl iodide by the Grignard reaction. It was dried over anhydrous potassium carbonate and purified by fractionation under diminished pressure. It boiled at 100–102° under 18 mm. Ethylphenylcarbinol was prepared in a similar manner from benzaldehyde and ethyl bromide. It distilled at 106–108° under 18 mm. Benzhydrol was prepared from benzaldehyde and phenyl bromide. It was purified by recrystallization from alcohol. It melted at 68°. Commercial benzene was fractionated 3 times with an 8-inch column. Only that portion which came over between 80° and 81° was used. The anhydrous aluminum chloride was a commercial product.

Methylphenylcarbinol, Benzene and Aluminum Chloride, I.—Fifty

[1] The use of a smaller amount of aluminum chloride did not materially affect the yield of triphenylmethane and the purification was more difficult because of a small amount of unchanged benzhydrol.

[2] *Compt. rend.*, 84, 1451 (1877).

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grams of methylphenylcarbinol were added to 40 g. of benzene. This mixture was cooled and constantly stirred by a motor. Aluminum chloride was added in small portions until 25 g. had been added. The temperature remained at 25–35° during the hour required for the addition of the dehydrating agent. The mixture became dark colored and pasty and developed a slight fluorescence. Much hydrochloric acid was given off. After standing 10 days the pasty mass was decomposed with ice water and extracted with ether. The ether extract was dried over calcium chloride. The ether was distilled off and the residue fractionated at atmospheric pressure.

THIRD FRACTIONATION.

125–150°,	2.0 g.
150–225°,	1.5 g.
225–300°,	15.1 g.
300–370°,	3.0 g.
Residues	23.2 g.

The fractions 125–150° from 3 experiments were combined and redistilled. Most of the distillate came over between 135° and 140°. It was oxidized with dilute nitric acid (10%). A good yield of benzoic acid (m. p. 120–121°) was obtained. The distillate was, therefore, ethylbenzene.[1]

The fraction 150–225° was mostly unchanged methylphenylcarbinol.

The fractions 225–300° from 2 experiments were combined and fractionated more than 20 times. One fraction, collected between 255° and 266°, weighed 4.1 g. Most of it came over at 260–263°. It solidified when cooled below 20° and had the odor and appearance of diphenylmethane. On oxidation with potassium dichromate and sulfuric acid it yielded benzophenone. Most of the remainder of the 225–300° fraction came over at 268–270°. When oxidized with chromium trioxide and acetic acid it yielded benzophenone. Analysis for carbon and hydrogen gave the following:

Subst. 0.1558; CO_2, 0.5301; H_2O, 0.1064.
Calc. for $C_{14}H_{14}$: C, 92.25; H, 7.74. Found: C, 92.72; H, 7.64.

It is, therefore, 1,1-diphenylethane.

Fraction 300–375°, on redistillation, partially solidified in the receiver. It was freed from adhering oil by pressing between filter papers, and sublimed. The sublimate melted at 212–215° and was oxidized with chromium trioxide and acetic acid to anthraquinone. This melted after recrystallization from acetic acid at 276–277°. Fraction 300–375° was therefore mostly anthracene.

Methylphenylcarbinol, Benzene and Aluminum Chloride, II.—Fifty g. of methylphenylcarbinol were mixed with 160 g. of benzene. The mixture was stirred and 35 g. of aluminum chloride were added in such portions

[1] Silva (*Loc. cit.*) obtained ethyl benzene as a by-product of the reaction between CH_3CHCl_2, C_6H_6 and $AlCl_3$.

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that the temperature did not rise above 35°. The reaction was quite smooth. Hydrochloric acid was given off and the mixture became dark colored due to the presence of a finely divided precipitate. This settled out slowly. After 5 days the mixture was decomposed with ice and dilute hydrochloric acid. The benzene portion was separated off, and the aqueous portion extracted with ether. The ether was distilled from the extract and the residue was added to the benzene portion. This was dried over calcium chloride and fractionated at atmospheric pressure.

FIFTH FRACTIONATION.

60–100°,	54.0 g.
100–150°,	4.0 g.
150–210°,	0.4 g.
210–300°,	22.6 g.
Residue	14.6 g.

Fraction 60–100° was found to consist largely of unchanged benzene. Fraction 100–150° came over mostly between 133° and 140° and was identified by the method already described as ethylbenzene. Fraction 150–210° had the odor of methylphenylcarbinol. Fraction 210–300° was repeatedly fractionated and was found to consist almost entirely of 1,1-diphenylethane. We were able to isolate but a small amount of anthracene from the residue.

Methylphenylcarbinol, Benzene and Aluminum Chloride, III.—The same weights of the alcohol and benzene were used as in the preceding experiment. The mixture was cooled in ice and treated with 33 g. of aluminum chloride. The temperature was kept below 10° except for a short time when it rose to 12°. After 8 days' decomposition, separation, extraction and fractionation were carried out as in the preceding experiment.

SIXTH FRACTIONATION.

60–100°,	110.0 g.
100–150°,	2.3 g.
150–210°,	4.1 g.
210–300°,	41.0 g.
Residue	6.2 g.

As before these fractions were found to consist of benzene, ethylbenzene, methylphenylcarbinol and 1,1-diphenylethane. No anthracene was isolated from the small tarry residue.

Ethylphenylcarbinol, Benzene and Aluminum Chloride, I.—Fifty grams of ethylphenylcarbinol were dissolved in 145 g. of benzene. While the solution was stirred 60 g. of aluminum chloride were added in such portions that the temperature remained between 35° and 40°. The mixture turned brick-red and then a very dark red. The last 20 g. of the chloride were added quite rapidly and caused very little increase in temperature. After standing 5 days at room temperature the mixture was decomposed with ice and dilute hydrochloric acid. The upper (benzene) layer was separated. The aqueous portion was extracted with ether and the residue from the

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ether extract was added to the benzene portion. After drying over calcium chloride this was fractionated.

TENTH FRACTIONATION.

60–120°,	117.0 g.
120–180°,	5.5 g.
180–225°,	5.6 g.
225–268°,	4.1 g.
268–300°,	16.1 g.
Residue	10.2 g.

The first fraction was unchanged benzene. Practically all of the second fraction (120–180°) came over at 159–162°. Dilute nitric acid oxidized it to benzoic acid. It was therefore, propylbenzene.[1] The third fraction distilled at 210–216°. It was identified by its odor and by oxidation to ethylphenylketone as unchanged ethylphenylcarbinol. The fraction 225–268° was identified as diphenylmethane. The last fraction came over at 273–275° at atmospheric pressure. Under 11 mm. pressure it distilled at 139°.[2] It was oxidized by chromium trioxide and acetic acid to benzophenone.

Subst., 0.1592; CO_2, 0.5361; H_2O, 0.1115.
Calc. for $C_{15}H_{16}$: C, 91.78; H, 8.22. Found: C, 91.83; H, 7.93.

It was therefore 1,1-diphenylpropane. The residue was heated in a distilling flask to 370°. About 4.6 g. of impure anthracene came over. This was purified by sublimation and identified by its melting point and oxidation to anthraquinone.

Ethylphenylcarbinol, Benzene and Aluminum Chloride, II.—Fifty grams of the alcohol and 150 g. of benzene were cooled in ice and treated with 30 g. of aluminum chloride. The dehydrating agent was added in such quantities that the temperature remained below 10° except for a brief period when it rose to 13.5°. After 12 days the mixture was decomposed with ice water and fractionated in the usual manner.

TENTH FRACTIONATION.

60–125°,	114.0 g.
125–180°,	4.6 g.
180–230°,	7.4 g.
230–268°,	2.2 g.
268–290°,	24.2 g.
Residue	8.4 g.

The fractions were identified as benzene, propylbenzene, ethylphenylcarbinol, diphenylmethane and 1,1-diphenylpropane, respectively. We were unable to isolate anthracene from the residue.

Benzhydrol, Benzene and Aluminum Chloride, I.—Twenty-five grams of benzhydrol were dissolved in 53 g. benzene and treated with 18 g. of

[1] Silva, *Loc. cit.*
[2] Klages, *Ber.*, 37, 1447 (1904).

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aluminum chloride in small portions. The reaction was quite vigorous and hydrochloric acid was given off rapidly. The temperature remained between 30° and 40° except for a brief period when it went to 45°.

After 3 days the dark-colored intermediate compound was decomposed with ice and dilute hydrochloric acid. It formed a semicrystalline yellow oil. The whole was extracted with ether. The extract was dried over calcium chloride and distilled. The temperature rose rapidly from 100° to 240°.

FOURTH FRACTIONATION.

240–275°,	3.2 g.
275–325°,	0.8 g.
325–370°,	13.7 g.
Residue (tar)	6.3 g.

The first fraction was identified as diphenylmethane. The third fraction solidified in the receiver. It was recrystallized from alcohol and identified by melting point, oxidation to triphenylcarbinol (m. p. 157–159°) and analysis as triphenylmethane.

Subst. 0.1662; CO_2, 0.5694; H_2O, 0.1004.
Calc. for $C_{19}H_{16}$: C, 93.39; H, 6.61. Found: C, 93.42; H, 6.74.

Benzhydrol, Benzene and Aluminum Chloride, II.—The condition of the previous experiment was duplicated, with the exception that the solution of benzhydrol was cooled in ice while the chloride was added. The temperature remained at 8° most of the time. It was never above 10°. After 3 days the mixture was decomposed and extracted with ether.

On distillation nothing came over between 120° and 290°. Between 290° and 330°, 1.8 g. of distillate came over which solidified in the receiver. After pressing between filter papers to remove the small amount of adhering oil (odor of diphenylmethane) the solid was recrystallized twice from alcohol. It melted sharply at 92–92.5°, the melting point of triphenylmethane. Between 330° and 370° (mostly 355–362°), 19.6 g. of crude triphenylmethane came over. After one crystallization from alcohol this melted at 91.5–92.5°. About 5 g. of residue remained in the flask.

Summary.

Secondary aromatic alcohols condense with benzene under the dehydrating influence of anhydrous aluminum chloride according to the following general equation:

$$\begin{matrix} C_6H_5 \\ R \end{matrix}\!\!>\!CHOH + C_6H_6 \xrightarrow{AlCl_3} \begin{matrix} C_6H_5 \\ R \end{matrix}\!\!>\!CHC_6H_5 + H_2O$$

When R is the phenyl group the reaction is smoother and a larger yield of the condensation product is obtained than when R is methyl or ethyl. The ethyl group has a greater retarding effect on the reaction than the methyl group.

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An excess of aluminum chloride tends to eliminate a phenyl or an alkyl radical from the product especially if the temperature is not kept low.

Since secondary alcohols of the type studied are easily prepared it is believed that the process will be of importance in synthetic organic chemistry.

EAST LANSING, MICHIGAN.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN.]

ON THE PREPARATION OF FORMAMIDE.[1]

BY ALBERT BRANN.

Received February 3, 1918.

In order to carry out a series of experiments on the linear velocity of the crystallization of formamide, it was necessary to use a product that had a definite melting point. Such a product apparently has not heretofore been prepared. Freer and Sherman,[2] who did a great deal of work on the preparation of formamide, determined its freezing point to be —1.0°. Davis and Putnam,[3] in their work on the conductivities of formamide and its solutions, very carefully distilled formamide that gave a minimum conductivity. However, they seem not to have determined the melting point of the formamide used by them, but quoted Walden,[4] who at different times obtained products with melting points varying between 1.5° and 2.1°. English and Turner[5] prepared formamide by fractional distillation that froze between 2.0° and 2.2°, a small sample freezing at the last named temperature. To show that the true melting point of formamide has been found, that it is a very definite thing, and to emphasize a few details regarding the preparation of formamide, are the objects of this paper.

Hoffman[6] discovered the fact that formamide is formed when ammonium formate is decomposed by heat. Freer and Sherman,[2] utilizing this reaction, worked out a very favorable method for its formation. However, the product with a freezing point of —1.0° produced by them was far from pure, probably due to the fact that they failed to distill off all the products of decomposition.

For the sake of clearness, the detailed operations in the preparation of formamide are given here. The operations are not new, but have been carried out and studied to a finality not hitherto accomplished.

[1] A portion of a thesis to be submitted to the Graduate School of the University of Wisconsin in partial fulfilment of the requirements for the Degree of Doctor of Philosophy.

[2] *Am. Chem. J.*, **20**, 223 (1898).

[3] Jones, "Conductivities and Viscosities in Solvents," *Carnegie Inst. Publication* 230.

[4] *Z. phys. Chem.*, **46**, 145 (1903); *Ibid.*, **55**, 230 (1906); *Ibid.*, **75**, 575 (1910).

[5] *Trans. Chem. Soc. J.*, **105**, 1656 (1914).

[6] *Ber.*, **15**, 980 (1882).

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A dry 3-liter round-bottomed flask was half filled with pure formic acid. The flask was connected directly to a Liebig's condenser which emptied into a filter flask, which, in turn, was attached to a tube through which excess ammonia vapors escaped. Dry ammonia gas was led into the formic acid through a glass tube reaching to the bottom of the flask, the gas first passing through two separate towers of stick caustic soda and soda lime. Considerable heat is evolved during the reaction. It is desirable to keep the contents of the flask at as low a temperature as possible, otherwise formic acid distills over, which combines with the ammonia in the condenser tube, forming crystals of ammonium formate. The flask was therefore immersed in cold running water. Fifteen to twenty minutes was sufficient time in which to neutralize all the formic acid. An inside coating, consisting of crystals of ammonium formate, collected on the cool parts of the flask while the rest of the salt remained melted. A bath of melted paraffin was now substituted for the water bath, and the ammonium formate gradually heated. The flow of ammonia gas was not interrupted during the whole process, except the rate of flow was somewhat diminished after the neutralization of the acid. At about 150° water of decomposition began to distill. The temperature was increased gradually to 180° at which temperature no more water distilled over. This operation usually took from 4 to 5 hours when starting with 1.5 liters of formic acid, but it is necessary to distill off all the water. It is desirable to do this at as low a temperature as possible in order to give the minimum decomposition of formamide. The resulting liquid should be brown in color. If the heating is continued too long or the temperature becomes too high, the liquid will be very dark brown or even black in color, a disadvantageous condition. The liquid was allowed to cool in the stream of ammonia gas.

This liquid was distilled under diminished pressure. The apparatus used was similar to that described so completely by Davis and Putnam.[1] The different distillates were colorless and had freezing points ranging from —2.0° to 0°. The combined distillates which froze at —1.1°, were allowed to stand over anhydrous sodium sulfate for 3 months. This was done because it was believed that the varying freezing points were due to the presence of water. This was probably not the case, however, but the impurities responsible for the variation, in all likelihood, were decomposition products; for at the end of the 3 months the formamide was again distilled under diminished pressure, and it was found that the freezing point of the resulting product had not materially changed. It was noticed, however, that during the first part of the distillation a few crystals of ammonium formate collected in the condenser tube. Accordingly, the middle portion of the first distillate was redistilled, whereupon the second product

[1] Jones, "Conductivities and Viscosities in Solvents," *Carnegie Inst. Publication* 230.

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of distillation gave a freezing point considerably higher than that of the first. Repeated fractional distillations brought up the freezing point higher and higher, till the fifth and sixth distillates gave identical freezing points, *i. e.*, 2.25°. New portions of the original formamide which had stood over sodium sulfate were fractionally distilled in the same manner

TABLE I.—TYPICAL RISE IN FREEZING POINT THROUGH FRACTIONAL DISTILLATION.

Fractional distillate.	Temperature of freezing point. ° C.
Original	—1.1
1	—0.2
2	+0.75
3	+1.45
4	+2.0
5	+2.25
6	+2.25

and the same final highest freezing point, 2.25°, was reached. From these results it was concluded that the important thing to do in order to obtain a pure product is to get rid of the volatile decomposition products, particularly the products of hydrolysis, by fractional distillation.

It should be stated regarding the yield of formamide that with so many distillations necessary to obtain a pure product, considerable loss in material was occasioned. The combined products from the first distillation of the brown liquid having a freezing point of —1.1° was 82% of the theoretical yield. By fractional distillation the final product freezing at 2.25° was 55% of the material freezing at —1.1°. The first and last portions of each distillate were combined and redistilled as before and an additional 25% of the material freezing at —1.1° was obtained pure. As a final pure product then approximately 66% of the theoretical yield was obtained.

The pure product is viscous, sticky to the touch, and neutral to litmus. A small sample of it was sealed off in a glass bottle, and has stood in a cupboard exposed to daylight and ordinary room temperatures for seven months. So far no discoloration or apparent change has taken place.

Formamide is hygroscopic, and workers with it have laid great stress upon this fact, being careful not to expose it to the air any more than necessary while using it. That the amount of error due to the taking up of moisture by short periods of exposure to the air is very slight, if any error is occasioned at all, is shown by the following facts: A given sample of formamide was exposed to the air by being poured from one flask to another during the distillation process 6 times. It was again exposed to the air in making up solutions; again in filling tubes from the flask containing the solutions; and again in transferring the used solutions to the distilling flask. On distilling off the formamide from such solutions, the first product of distillation gave the highest freezing point, 2.25°, showing

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that the exposures to the air had not interfered with the purity of the solvent. These facts do not belittle the care which should be taken to keep away moisture, for slow hydrolysis takes place when formamide is exposed to water, the products of hydrolysis being ammonia and formic acid, substances which do materially lower the freezing point, as pointed out by Freer and Sherman.[1]

Summary.

The important facts upon which this paper wishes to lay emphasis are the following:

1. The freezing point of formamide has been found to be 2.25°, which is the highest freezing point so far obtained for it, and which is probably the true freezing point of the pure substance.

2. Formamide can be obtained pure and is best freed from its products of decomposition and hydrolysis by fractional distillation.

3. Although formamide is hygroscopic in nature, when reasonable care is exercized regarding its exposure to the air, moisture is not taken up in quantities great enough to interfere with its purity as determined by its freezing point.

MADISON, WISCONSIN.

[CONTRIBUTION FROM THE LABORATORIES OF THE OFFICE OF SOIL FERTILITY, BUREAU OF PLANT INDUSTRY, UNITED STATES DEPARTMENT OF AGRICULTURE.]

THE ACTION OF NEUTRAL SALTS ON HUMUS AND OTHER EXPERIMENTS ON SOIL ACIDITY.

BY LOUIS J. GILLESPIE AND LOUIS E. WISE.

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Introduction.

The action of neutral salts on soils is an interesting one, and has been the subject of numerous investigations, the aim of which in many cases was to measure the quantity of acid substance in soils and to determine the nature of soil acidity. There are undoubtedly many soils of so-called acid character, from which very little acid can be extracted with water, in many cases so little that the water extracts are not observed to turn litmus paper. The acidic nature is manifested, however, in other ways. The soil may (1) affect vegetation in certain characteristic ways, (2) give a water extract which does not react alkaline to phenolphthalein when the carbon dioxide is removed by boiling, even after small quantities of lime have been added to the soil, (3) act on neutral salts with the development of appreciable quantities of acid, and (4) act readily on litmus paper if the paper is brought into intimate contact with the moist soil. These manifestations are not always perfectly correlated, but whenever evident, they may be caused to disappear by adding sufficient lime or other basic material.

[1] *Am. Chem. J.*, 20, 223 (1898).

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At first sight there would seem to be no doubt that such soils, which can at least be described as acidic in a general sense, actually contain acid substances. Closer scrutiny of some of the phenomena, especially the action of salts on soils and the litmus test, has led to the conclusion that such manifestations do not prove the presence of "true acids," and some workers have gone further and have concluded that "truly acid" soils do not exist, save in the few cases where the water extract turns litmus paper.

Now the characteristic effects of acid solutions are due mainly to the preponderance of hydrogen ions over hydroxyl ions. This preponderance is regulated entirely by the hydrogen-ion concentration at any given temperature and can not be found by measuring the titratable acidity in complicated mixtures such as soils, even if the titer could be accurately determined. One of us[1] showed, however, that when soils of various type and origin are treated with water, extracts can be obtained which possess experimentally definite hydrogen-ion concentrations. A centrifuge was used, and filtering avoided. Such extracts, though they are not usually observed to turn litmus paper (without special precautions), turn more brilliant indicators when these are used in solution rather than on paper. By the use of these indicators it was found possible to measure the hydrogen-ion concentration of each soil extract, generally with two different indicators. The results so obtained agreed well with each other and with hydrogen-electrode measurements of the soils in suspension.

Some of the hydrogen-ion concentrations reported were pointed out as being rather high from a biological point of view. Since then numerous other soils have been found which show hydrogen-ion concentrations close to or even higher than the point where many bacterial species suffer injury. Sharp and Hoagland[2] found such soils, using an electrometric method very similar to that used in this laboratory. Gillespie and Hurst[3] found that such soils are very common in northern Maine, and were led to suggest that the relatively high hydrogen-ion concentration of the Caribou loam might be responsible for its relative freedom from potato scabs, a suggestion which has been strongly supported in the case of the common potato scab by a study, soon to be published elsewhere, of the growth of the causal organism at different hydrogen-ion concentrations. The existence of such soils would seem to place beyond question the widespread occurrence of "truly acid" soils, the acidity of which is *biologically* significant.

Sharp and Hoagland state "the work of Gillespie, paralleled by that presented in Table II, conclusively proves that there may be an excess of H ions in the solution bathing the soil particles." They also state that it is not necessary to associate soil acidity with physical adsorption.[4]

[1] Gillespie, *J. Wash. Acad. Sci.*, 6, 7 (1916).

[2] *J. Agr. Res.*, 7, 123 (1916).

[3] *Soil Science*, 4, 313 (1917).

[4] It may be well to note that both Gillespie, and Sharp and Hoagland, found

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Nevertheless, soil acidity has long been associated with adsorption, and the action of neutral salts on soils and the behavior of litmus paper with soils and with soil extracts appear to offer special difficulties.[1]

We wish, therefore, to describe some experiments on the action of the so-called humus on neutral salts and on the behavior of litmus paper toward various acid solutions, and to discuss the bearing of such experiments on the nature of soil acidity.

The Action of Humus on Neutral Salts.

Sharp and Hoagland found by means of the hydrogen electrode that the hydrogen-ion concentration of extracts of acid soils prepared with neutral chlorides is greater as a rule than that of extracts prepared with water. Barium chloride was more active than sodium or potassium chloride. Previous to this work we had regarded with suspicion many investigations on the titratable acidity of salt extracts of soil, since in many cases no mention was made of the purity of the salt used, and the presence of any salts of weak acids would have robbed the results of much of their significance, because an increase of hydrogen-ion concentration was not shown, but only inferred. We have also seen the effect of sodium chloride and sodium acetate on soils by the use of indicators, and have found that a soil may yield on extraction with sodium acetate much more titratable acid than on extraction with sodium chloride (this is the usual finding), and the hydrogen-ion concentration be the higher in the sodium chloride extract. When different concentrations of sodium acetate are used, it is found that the smaller the concentration, the smaller is the quantity of titratable acid liberated, but the greater is the hydrogen-ion concentration. This suggested that this process, though not necessarily purely chemical, as maintained by Truog,[2] has its chemical aspect, since it seems to be limited by high hydrogen-ion concentrations. In extending this work we chose humus rather than soil, and treated it with varying quantities of potassium, sodium or barium chloride, to find out whether there was any limiting hydrogen-ion concentration. There was no indication that the process was not practically instantaneous.[3]

certain so-called alkali soils to yield extracts which were alkaline without boiling off carbon dioxide. The term alkali soil signifies a soil containing salts of the alkali metals, and has no reference to alkalinity, except in the case of the so-called black alkali. Hoagland has recently reported experiments which suggest strongly that the relatively feeble degrees of alkalinity observed by the above workers may have however a distinct biological significance. (*Soil Science*, **3**, 547 (1917).)

[1] J. E. Harris, *J. Phys. Chem.*, **21**, 454 (1917).

[2] *J. Phys. Chem.*, **20**, 457 (1916).

[3] We chose humus rather than soil for this purpose because humus extracts offer no such difficulties to electrometric measurement as are often offered by soil extracts. Such difficulties are stated by Sharp and Hoagland to be due to the nitrate content of soils; we confirmed this practically quantitatively for one soil by comparing the behavior of the extract with that of known solutions of the same buffer action and nitrate

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Electrometric Measurements.—The measurements were made in a Clark electrode vessel provided with the modified three-way stopcock suggested by Cullen.[1]

The electrode vessel was filled with hydrogen, then partly filled with the fluid to be tested, and shaken mechanically for 5 minutes to bring about equilibrium. The shaking was then stopped, the liquid contact with saturated potassium chloride solution made with mixing, in a tube about 7 mm. in internal diameter, and the total potential measured at once with an accurate potentiometer of the low resistance type, against a well seasoned and tested saturated potassium chloride calomel electrode. In all the tables the potential recorded is this total potential difference, in millivolts. The platinum electrode was always freshly coated with palladium black after removal of the previous coating by nitric acid, and in the usual way washed with distilled water, subjected to cathodic polarization in dil. sulfuric acid, and washed again abundantly. According to Cumming and Gilchrist[2] and Clark and Lubs,[3] absolutely constant potentials are not in general observed, or to be expected, but the most reproducible and reliable value is obtained soon after liquid contact is made. As a rule the potential varies a little after liquid contact is made, but the change in 5 minutes is ordinarily small. In most cases we observed the changes after 5 minutes, the vessel not being shaken after the first measurement, and the electrode being totally immersed in the liquid. When the potential was inconstant will be noted below. The measurements were made in a constant temperature compartment provided with electrical temperature control set at 30°; for most of these experiments the electrical control was not used, but the temperature only slowly changed with the room temperature, generally changing not more than 0.5° in half a day, and the inconstancies of potential could not have been due to the temperature variations.

Orienting Experiments.—Humus was prepared from Scottsburg silt loam from Indiana as follows: The soil was extracted with 2% sodium hydroxide solution, the silt allowed to settle, the alkaline liquor siphoned off and treated with enough sulfuric acid to cause the formation of a brown flocculent precipitate. This was filtered off, redissolved in 1% sodium hydroxide, the solution filtered from residual silt and again acidified with sulfuric acid. The precipitate thus obtained was once more "purified" by the above procedure. Washed repeatedly with distilled water with the aid of a centrifuge, the preparation, which at first yielded clear supernatant fluids, began to go into colloidal solution and yielded increasingly denser

content. Very dilute sulfuric acid solutions were used for this. Solutions of greater buffer action do not show much disturbance due to such quantities of nitrates.

[1] Clark, *J. Biol. Chem.*, **23**, 475 (1915).

[2] *Trans. Faraday Soc.*, **9**, 174 (1913).

[3] *J. Biol. Chem.*, **25**, 479 (1916).

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and more colored washings. After two washings the hydrogen-ion exponent (p_H of Sörensen) was determined neglecting diffusion potentials[1] and found to be 3.6; after 4 washings, 4.1; and after five, 4.15. After 5 washings a portion of it was washed with normal potassium chloride solution; the humus was precipitated, leaving the supernatant fluid water-clear, and the supernatant fluid had the exponent 3.3. On washing further with normal potassium chloride the exponent increased very slowly, reaching after the eighth washing the value 4.65. Some of the humus treated with potassium chloride was treated with dil. sulfuric acid to extract potassium, and washed 6 times with water, until the exponent of the last wash-water was 4.55, and when this material was then treated again with normal potassium chloride it yielded a supernatant fluid, the exponent of which was 3.26.

The original humus preparation was reprecipitated once more with sulfuric acid from alkaline solution, washed 4 times with water, until the last washing showed the exponent 4.1 and contained considerable quantities of humus, and then the humus was treated with normal potassium chloride. The exponent of the clear fluid resulting was then 3.46. The concentration of humus was not controlled well in these experiments, but the process seemed to a considerable degree both reproducible and capable of reversal.

Further Experiments.—In further experiments the procedure was the following: Ten cc. of humus suspension were treated with 10 cc. of saline solution of the desired concentration, the mixture permitted to settle a few minutes or centrifuged, and a portion decanted and examined electrometrically. In all cases the addition of salt precipitated the humus from its suspension or colloidal solution more or less completely. In the last experiment (No. 5) 10 cc. of a given mixture containing no humus were treated with the same volume of saline solution and the mixture examined. In all cases the concentrations reported for humus, salt, or other substance are calculated for the 20 cc. of mixture, assuming no change of volume on mixing. Since the Bjerrum extrapolation does not in general determine the diffusion potentials with certainty we have preferred to report all the results in terms of the total potential, rather than to apply the corrections for diffusion potentials and to calculate the hydrogen-ion exponents. Neglecting diffusion potentials, a decrease of total potential of 10 millivolts would correspond to a decrease of about 0.17 in the value of the exponent.

[1] The diffusion potentials of the supernatant fluids from this humus were estimated according to Bjerrum's principle (see Walpole, *J. Chem. Soc.*, 105, 2501 (1914)) and found to be 2 or 3 millivolts or less for the water suspensions, and less than 0.1 millivolt for the potassium chloride extracts. They were neglected in calculating the exponents.

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Experiment 1.—The humus was prepared from Superior clay, a soil from Wisconsin, as follows: The soil was treated with 2% sodium hydroxide solution and the crude humus precipitated by acetic acid. The precipitate was redissolved in 1% sodium hydroxide solution, the silt filtered off, and the humus precipitated with acetic acid, washed with distilled water, and dried at 50°. This humus yielded 25.3% of ash, which contained carbonates, was strongly alkaline, and contained a large quantity of aluminium, a small quantity of iron, and traces of calcium. The humus contained 3.7% nitrogen, on the ash-free basis. Another reprecipitation of the humus did not affect appreciably the ash or nitrogen content. For use, the dried humus was once more dissolved in 1% sodium hydroxide solution, precipitated with acetic acid, washed sufficiently free from acid with the aid of a centrifuge, and suspended in distilled water. The mixtures represented 0.85% of humus. The results, obtained at 21°, are given in Table I.

TABLE I.—COMPARATIVE EFFECTS OF SODIUM AND BARIUM CHLORIDES ON HUMUS FROM SUPERIOR CLAY SOIL.

Salt.	Concentration in gram equivalents per liter.	Potential in millivolts.	Change of potential due to salt.
NaCl	0	546.5	..
	0.17	512.20	—34.3
	0.43	507.80	—38.7
	0.86	504.45	—42.0
	1.71	499.80	—46.7
	3.10	499.45	—47.0
$BaCl_2$	0	546.5	..
	0.007	508.0	—38.5
	0.04	499.2	—47.3
	0.14	495.5	—51.0
	0.21	495.7	—50.8
	0.36	496.5	—50.0
	0.72	496.8	—49.7

Table I shows large decreases in the value of the potential due to the addition of sodium or barium chloride to the humus suspension; these decreases of potential point to considerable increases of acidity. Neglecting diffusion potentials the hydrogen-ion exponent of the humus plus water was 5.1, of the distilled water, 6.2; and of 4 *M* sodium chloride solution, 7.7. The electrometric measurements of half-saturated barium chloride gave erroneous results as shown by indicator tests and as indicated by the electrometric behavior. The potentials drifted badly, as much as 9 millivolts in 5 minutes. The barium chloride solution was however certainly less acid than the humus itself. The mixtures of barium chloride and humus behaved much better, the drifts being about 1 millivolt in 5 minutes. The mixtures with sodium chloride showed drifts of about 0.3 millivolt in 5 minutes.

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Measurements were also made with 0.17 and 1.7% humus, which need not be reported in detail. The results showed that the potential was lower, the more concentrated the humus. The lowest potential observed was 489 millivolts, found for a mixture of equal volumes of 3.4% humus and saturated barium chloride solution.

Experiment 2.—In this and the rest of the experiments potassium chloride, recrystallized from distilled water, was used instead of sodium chloride, and the barium chloride was recrystallized. The humus mixtures with the recrystallized barium chloride behaved very well, showing changes of potential of only 0.2 millivolt or less in 5 minutes; the behavior of the humus mixtures with potassium chloride was equally satisfactory. Solutions of either potassium or barium chloride without humus showed inconstant potentials which were only very roughly reproducible; the potentials however agreed with indicators in showing the solutions to be nearly neutral, compared with the humus suspensions. Such unsatisfactory electrometric behavior of neutral salts seems characteristic; the buffer action of many impurities would secure better behavior. Mixtures rich in neutral salts and poor in buffer action are very easily polarized. The temperature was electrically controlled at 30.0°. The results are given in Table II.

TABLE II.—COMPARATIVE EFFECTS OF POTASSIUM AND BARIUM CHLORIDES ON HUMUS FROM SUPERIOR CLAY SOIL.

Salt.	Concentration in gram equivalents per liter.	Potential in millivolts.	Change of potential due to salt.
KCl	0	537.7	..
	0.02	524.4	—13.3
	0.10	514.15	—23.5
	0.40	508.4	—29.3
	1.00	504.95	—32.7
	2.00	501.7	—36.0
$BaCl_2$	0	537.7	..
	0.01	506.5	—31.2
	0.06	499.3	—38.4
	0.25	495.6	—42.1
	0.62	492.1	—45.6
	1.24	486.4	—51.3

Experiment 3.—A dried preparation of humus from Volusia silt loam was dissolved in dil. sodium hydroxide solution, filtered, then treated with conc. hydrochloric acid and the resulting precipitate washed on the filter. When the humus was washed by the use of a centrifuge the supernatant fluid obtained was itself a heavily colored colloidal solution. A sufficient volume of this solution was filtered through paper and used for the experiment. On filtering, the material passed through the paper, leaving only a slight stain, which also passed through when washed with a little distilled water.

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Ten cc. of colloidal solution were treated with a mixture of 0.5 cc. of 30% potassium chloride solution plus 9.5 cc. of distilled water. The humus appeared to be completely precipitated, leaving the supernatant fluid clear but not quite colorless. This fluid showed a potential 21 millivolts lower than that shown by 10 cc. of colloidal solution plus 10 cc. of water. When 10 cc. of colloidal solution was treated with a mixture of 9.5 cc. of the potassium chloride solution and 0.5 cc. of water, the supernatant fluid obtained was quite colorless and showed a potential 16 millivolts lower than that found when the smaller quantity of potassium chloride was used. To determine whether this additional change of 16 millivolts was due to a continued reaction of potassium chloride with humus already precipitated, we treated the colloidal solution with potassium chloride solution in the proportions: 10 cc. colloidal solution plus the smaller quantity of potassium chloride solution (0.5 cc.), and removing the precipitated humus before making up the volume to 20 cc., then, taking 10.5 cc. of the supernatant fluid from this precipitation, we made up the volume in one case with 9.5 cc. of distilled water and in another case with 9.5 cc. of the potassium chloride solution. We found then that of these two preparations the one with more potassium chloride showed a potential 12.5 millivolts lower than the other. Considering that the humus was not precipitated in quite the same concentration, and that a little more humus was precipitated on the addition of the larger quantity of potassium chloride, it appears that nearly the same change of potential is produced by the increase of potassium chloride whether the mass of humus is present or not; in other words the continued effect on the potential of the larger quantities of potassium chloride, after the precipitation is practically complete, is not due to a continued reaction with precipitated humus, but mainly to something else, (possibly to effects such as those which are the subject of Expt. 5). The experiment, performed at 23°, is given in Table III. The supernatant fluid mentioned in the table is the one obtained by treatment of 20 cc. of colloidal solution with 1.0 cc. of the 30% potassium chloride solution and centrifuging. In the table, "KCl" means the 30% solution. All the mixtures were centrifuged before testing.

TABLE III.—PROTOCOL OF EXPERIMENT 3.

No.	Mixture.	Potential in millivolts.	Potential after 5 minutes.
1	10 cc. colloidal solution + 10 cc. H_2O	449.2	448.9
2	10 cc. colloidal soln. + (0.5 cc. KCl + 9.5 cc. H_2O)	428.15	428.10
3	10 cc. colloidal soln. + (9.5 cc. KCl + 0.5 cc. H_2O)	412.25	412.15
4	10.5 cc. supernatant fluid + 9.5 cc. H_2O	434.50	434.40
5	10.5 cc. supernatant fluid + 9.5 cc. KCl	422.05	422.00
6	10 cc. H_2O + 10 cc. KCl	587.0	613.0

Experiment 4.—A colloidal suspension was prepared from the same material as that used in the previous experiment, and the comparative effects

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of potassium chloride and barium chloride on it were studied as in Expts. 1 and 2, and all the diffusion potentials were estimated by the Bjerrum extrapolation. The measurements were made at 24°. The results are shown in Table IV.

TABLE IV.—COMPARATIVE EFFECTS OF POTASSIUM AND BARIUM CHLORIDES ON VOLUSIA HUMUS.

Salt.	Concentration in gram equiv. per liter.	Appearance of supernatant fluid.	Potential in millivolts.	Potential after 5 minutes.	Change of potential due to salt.	Diffusion potential correction in millivolts.
0.....	0	thick	463.5	463.1	..	—0.4
KCl.....	0.02	thick	449.45	449.40	—14.0	—0.15
KCl.....	0.2	clear but yellow	441.35	441.25	—22.1	—0.05
KCl.....	1.0	very light color	434.30	434.25	—29.2	—0.03
$BaCl_2$.....	0.02	still less color	436.85	436.85	—26.7	—0.05
$BaCl_2$.....	0.2	almost no color	430.30	430.35	—33.2	+0.83
$BaCl_2$.....	1.0	same	420.70	420.70	—42.8	+2.0

As in Expt. 2, barium chloride exerts a considerably greater effect than potassium chloride at equivalent concentrations on the potential and also on the precipitation of the humus. Some of the difference in the effects on the potential is due however to diffusion potential, but how much may be due to this can not be stated at present, since the Bjerrum extrapolation may not be exact for these mixtures, though the sign of the correction is probably reliable. Fairly large differences were seen by Harned in the action of potassium and barium chlorides on the hydrogen electrode potential of decinormal hydrochloric acid; these differences were attributed by him to differences of diffusion potential (he did not apply the method of Bjerrum, but calculated the diffusion potentials).[1]

The fact that such differences can be observed in the absence of colloidal or undissolved substance makes it unsafe to conclude that the barium reacts more extensively with the humus than does potassium. The same applies to sodium.

Experiment 5.—A number of solutions were tested in an effort to find a mixture which would give with potassium chloride effects on the hydrogen electrode potential comparable with those seen in the case of humus. The procedure was similar to that used for the humus preparations; 10 cc. of the given mixture were treated with 10 cc. of potassium chloride solution. The results are shown in Table V. The concentrations of potassium chloride and other substances entered in the table are those calculated for the mixture examined, assuming no change of volume to occur on mixing. The mixtures were not prepared with precision, but the results are comparable with those obtained with humus. As in the previous cases, the total potential observed between the hydrogen electrode and the saturated potassium chloride calomel electrode is given in millivolts.

[1] THIS JOURNAL, 38, 1986 (1916). The calculation in our case can not be made.

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TABLE V.—EFFECT OF POTASSIUM CHLORIDE ON THE HYDROGEN ELECTRODE POTENTIAL (INCLUDING DIFFUSION POTENTIAL) OF VARIOUS SOLUTIONS.

	Mixture.	KCl, mols per liter.	Potential in millivolts.	Potential after 5 minutes.	Change of potential due to salt.	Diffusion potential correction, in millivolts.
1	0.102 *N* HCl	0	312.55	312.45	..	—3.4
		0.1	312.20	312.05	— 0.3	—3.25
		1.0	309.40	309.25	— 3.1	—2.0
		2.0	301.40	301.15	—11.1	—1.55
2	0.001 *N* HCl	0	446.3	446.6	..	—0.3
		0.1	445.65	445.70	— 0.6	0.0
		1.0	442.25	442.25	— 4.0	..
		2.0	438.70	437.95	— 7.6	0.00
3	0.01 *N* H_2SO_4	0	373.4	373.55	..	+0.3
		0.2	372.2	..	— 1.2	..
		1.0	367.75	367.70	— 5.7	—0.25
4	0.001 *N* H_2SO_4	0	428.5	428.5	..	..
		0.2	427.55	..	— 1.0	..
		1.0	426.8	..	— 1.7	..
		2.0	419.3	418.8	— 9.2	..
5	0.013 *N* $Al_2(SO_4)_3$, 0.0005 *N* H_2SO_4	0	473.2	47315	...	0.0
		0.2	477.9	..	+ 4.7	0.0
		0.8	482.5	482.8	+ 9.3	..
		2.0	476.5	478.5	+ 3.3	0.0
6	0.05 *M* H_3BO_3, 0.0085 *N* NaOH	0	745.8	746.0	..	—0.2
		0.2	737.40	737.60	— 8.4	—0.2
		0.8	731.80	732.10	—14.0	—0.05
		1.4	729.45	729.80	—16.3	..
		2.0	727.65	727.95	—18.1	0.0
7	0.05 *M* H_3BO_3	0	613.0	614.0	..	—1.4
		0.2	577.0	582.0	—36.0	—0.05
		0.8	614.0	629.0	+ 1.0	0.0
		1.4	616.0	628.0	3.0	0.0
		2.0	603.0	622.0	—10.0	0.0
8	0.05 *M* H_3BO_3, 0.00002 *M* H_2SO_4	0	530.1	530.7	..	..
		0.2	519.8	521.8	—10.3	..
		1.0	581.5	604.0	+51.4	..
		2.0	561.0	593.0	30.9	..
9	0.05 *M* H_3BO_3, 0.005 *M* H_2SO_4	0	372.0	372.15	..	—0.1
		0.2	371.9	..	— 0.1	..
		1.0	367.05	367.50	— 5.0	—0.25
10	0.067 *M* phosphate	0	518.65	518.45	..	—0.4
		0.2	507.80	508.25	—10.8	—0.3
		1.0	505.0	505.0	—13.6	—0.2
		2.0	500.0	502.0	—18.6	..
11	0.0067 *M* phosphate	0	541.3	544.0	..	..
		0.2	523.2	527.1	—18.1	..
		1.0	536.0	546.0	— 5.3	..
		2.0	525.0	541.0	—16.3	..

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The first set of mixtures, which were 0.102 N with hydrochloric acid and contained varying concentrations of potassium chloride, gave results close to Harned's precise results for 0.1 N hydrochloric acid, except that the change of potential found here for 2 mols of potassium chloride is somewhat higher. In the second set the concentration of the acid is smaller, 0.001 N, but the effects are of the same order of magnitude, compared with the larger humus effects, as may be seen in Fig. 1. Mixtures 3 and 4 contained two concentrations of sulfuric acid, and the effects are about as large as those shown by hydrochloric acid. Mixture No. 5 contained aluminum sulfate, filtered clear, and a trace of sulfuric acid added; the changes of potential were of opposite sign to those of the rest of the mixtures, and pointed to a decrease of hydrogen-ion concentration. The next four mixtures contained 0.05 mol of boric acid per liter but had different initial hydrogen-ion concentrations, and because of this fact they should also possess different buffer capacities—in fact No. 6 and No. 9 should have a considerable buffer action, whereas Nos. 7 and 8 should have very little. Corresponding to these differences were great differences in electrometric behavior: Nos. 6 and 9 were capable of satisfactory measurement; and Nos. 7 and 8 showed very serious drifts of potential in 5 minutes after the first measurement, and the changes of potential due to addition of potassium chloride were apparently very high, but very irregular and of course uncertain because of the inconstancy of the potential. Mixture No. 6, of partially neutralized boric acid, showed fairly high effects: these are not shown in Fig. 1 in part because such a mixture could not be present at the hydrogen-ion concentrations of the humus preparations and also because as large effects were seen in the case of Mixture No. 10. Mixtures 10 and 11 were examined because Palitzsch reported, incidentally in his study of methyl red,[1] large effects on the hydrogen-ion concentration of "0.25 sec." phosphate mixtures when sodium chloride was added; the effects were of

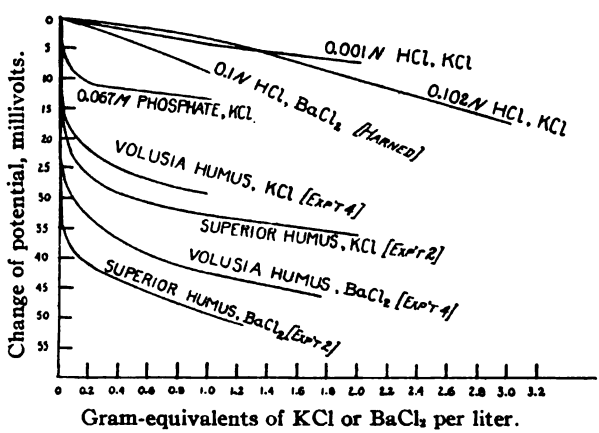

Fig. 1.—Changes of potential resulting from the action of salts on humus or on solutions. A drop in the curve means a fall in the potential.

[1] *Biochem. Z.*, 37, 131 (1911).

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the same order of magnitude as our humus effects. The same mixture of phosphates was used by us in these experiments, *i. e.*, Na_2HPO_4 and KH_2PO_4 in the molecular ratio 0.25 to 9.75, and the final phosphate concentrations, after addition of the potassium chloride solution, were the same as in his experiments. In the case of mixture No. 10, the electrometric behavior was satisfactory; such a mixture could exist at the hydrogen-ion concentrations of the humus preparations, and the effects are fairly large, as shown in the figure. In the case of the more dilute mixture, No. 11, the effects are about as large, but irregular, and the potential inconstant.

Fig. 1 shows the comparative effects of potassium and barium chlorides on humus preparations and on some solutions. Harned's values for the effect of barium chloride on 0.1 *N* hydrochloric acid are also given. Diffusion potential corrections were not applied in any case. Not all the results can be clearly shown in one figure, but the most significant results are shown. It may be well to note that the curve for Superior clay humus and sodium chloride would very nearly coincide with the curve shown for Volusia humus and barium chloride, so that with the Superior clay humus the spread of the curves for the three salts resembles the spread of the curves found by Harned for 0.1 *N* hydrochloric acid and the same three salts.

There seems to be no reason to doubt that the large decrease of potential seen when potassium chloride is added to humus is due to a large increase of hydrogen-ion concentration, which in turn is due mainly to a reaction between the potassium chloride and the humus. The action of salts on the hydrogen-ion activity of true solutions and the uncertainties due to diffusion potentials make it difficult to draw any conclusions as to the mechanism of the reaction between salts and humus.

The mechanism of the reaction between soils and neutral salts is in dispute. Harris maintains that when a portion of soil is repeatedly extracted with saline solution, the total acid substance yielded by sodium chloride or potassium nitrate is very much less than that yielded by sodium acetate.[1]

He mentions a difference in the total acid yielded by potassium nitrate and sodium chloride (this difference is small compared with the difference seen by him in the action of ether and sodium acetate), and points out that it is difficult to account for the liberation of so much acid on the assumption that the reaction is purely chemical, and insists that it is a case of adsorption, following the typical adsorption curve. It is fair to point

[1] *J. Phys. Chem.*, **18**, 355 (1914); **21**, 454 (1917). The total acid substance can not of course be actually measured, because only a certain fraction is given off at each treatment, but the totals may be comparatively estimated for different salts by comparing the rates. Such an experiment would seem to demand careful attention to technique, especially with regard to endpoint because of the buffer action of strong solutions of sodium acetate, in order that no accumulative error be introduced at each titration. No difficulties were reported by Harris.

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out that the fact that sodium acetate reacts so much more extensively with soil than does potassium nitrate or sodium chloride (in a single treatment) may well be due to the buffer action of sodium acetate, which permits the liberation of a considerable quantity of acetic acid without too high a hydrogen-ion concentration resulting. We also appreciate the difficulty of accounting for the large apparent increase of hydrogen-ion concentration occurring when humus is treated with potassium chloride, on the assumption that the process is purely chemical, but we do not seek to draw a sharp line between chemical and adsorptive processes.

Even if such a sharp line could be drawn, and the liberation of acid from neutral salts by soils or humus be placed in a category of purely adsorptive processes, we do not see how this would indicate the absence of truly acid bodies in soils that exhibit the adsorptive property. Truly acid and adsorptively unsaturated bodies may be present together, and indeed probably are. The fact given by Harris that repeated extraction of soils with saline solutions gives different total results according to the nature of the salt would go to show that we can not sharply titrate in this (indirect) way the quantity of acid substance. It is common knowledge that different methods of determining lime requirements (these are titrimetric methods in principle) give different results, and this of itself has led to the suspicion that the acidity of soils is of a peculiar kind, and not a "true acidity." Truog[1] maintains that soils may be titrated with various bases with the same result, or treated with various chlorides with the liberation of equal quantities of acid, if suitable experimental conditions be chosen. Harris replies in effect that the personal equation enters into the choice of conditions.[2] It is time to recognize that titratability is not a criterion by which the presence of true acids in all mixtures can be tested. We know from the modern theory of titration[3] that acids can not always be titrated in mixtures. Thus acetic acid can not be accurately titrated in mixture with any substance having a large buffer effect at the turning point of phenolphthalein, nor can the total quantity of acid substance always be titrated in such mixtures. It is apparent that the behavior of soils toward attempts to determine the quantity of acid substance offers no evidence whatever against the presence of true acids in the so-called acid soils.

These considerations do not discredit the usefulness of such titrimetric methods as that of Veitch. Such a method is capable of determining the quantity of lime which must be added to bring a soil to an approximately neutral condition, if neutrality is considered not in the stoichiometrical sense, but in the physico-chemical sense. Whether such methods can serve to solve fundamental problems of soil fertility is doubtful, since

[1] *Loc. cit.* and *J. Ind. Eng. Chem.*, **8**, 341 (1916).

[2] *J. Phys. Chem.*, **21**, 454 (1917).

[3] See for instance Hildebrand, THIS JOURNAL, **35**, 847 (1913).

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titrimetric methods have been found insufficient in other fields of applied biology, notably bacteriology.[1]

It is of course true, as suggested by Harris, that the small quantity of acid which is extracted from soils by water and detected by means of the hydrogen electrode (or by suitable indicators) can not be the *cause* of the liberation of the large quantities of acid when the soil is treated with a salt. Neither can it be the cause of the binding of large quantities of lime or other bases. Actually, the hydrogen-ion concentration of soil extracts is *dependent* in high degree on the undissolved acidic or adsorptively unsaturated substances, and if these are permitted to bind large quantities of lime or other bases, the soil extract which may then be obtained will have a very different hydrogen-ion concentration. In any case, with mixtures such as soil, the hydrogen-ion concentration can not in general be said to be *due* to any one acid substance, and, since soil acidity has a manifold connotation, we can not safely make at this time any broad statements as to the "cause of soil acidity."

The Behavior of Litmus Paper.

The fact that water extracts of many soils apparently fail to turn litmus paper, though the litmus paper may promptly be turned if pressed into close contact with the moist soil, has led to the statement that the action is a purely adsorptive process and therefore incapable of demonstrating acidity in a chemical sense. The further conclusion has also been drawn that truly acid soils do not in fact exist, save in the rare cases where the litmus paper is turned by the soil extract. Ramann[2] for instance substitutes the term "adsorptively unsaturated" for the term "acid" soil.

The view that when soil acts on litmus paper the soil selectively adsorbs the base of the blue litmus salt, leaving the red dye on the paper, has recently been stated by Harris[3] to constitute a plausible explanation of the action. It seems to us that some such explanation is conceivable but hardly plausible, as the actual mechanism of the process would offer difficulties. Furthermore there is no logical necessity of giving one and the same explanation for the action of litmus paper and the action of neutral salts on soils. The behavior of litmus paper can be explained in a simple way by means of the following experiments, which illustrate strikingly some of the principles involved in the application of litmus paper, principles which have been discussed in a very thorough manner by Walpole.[4]

We prepared a solution containing 0.5 cc. of 0.2 N hydrochloric acid per liter, *i. e.*, a 0.0001 N solution, using ordinary distilled water. When 5 cc. of this solution were treated with 2 drops of an aqueous solution of methyl

[1] See Clark and Lubs, *J. Bact.*, **2**, 1, 109, 191 (1917).

[2] E. Ramann, "Bodenkunde," 3rd edition, Berlin, 1911.

[3] *J. Phys. Chem.*, **21**, 454 (1917).

[4] *Biochem. J.*, **7**, 260 (1913).

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red[1] a red color instantly developed, which enabled us to measure the hydrogen-ion concentration in the usual way, by comparison with standards. The hydrogen-ion exponent was found to be 4.8.[2] When strips of Squibb's sensitive neutral or the blue litmus paper were placed in the hydrochloric acid solution, *no changes*, relative or absolute, could be observed in the papers at the end of 5 minutes, a control experiment also being performed with distilled water. The acid solution showed a faint pink tinge due to the leaching of the litmus coloring matter. At the end of 13 minutes, both papers in the acid solution had acquired only a slight pink tint around the edges. When however neutral and blue litmus paper strips were placed in $M/20$ *phthalate buffer mixtures* having a hydrogen-ion exponent of 4.8, they were instantly reddened.

The contrast was even more striking in the case of another solution which was prepared by diluting one drop of 0.2 N hydrochloric acid to one liter. Colorimetric test of this solution with methyl red showed an exponent of 6.1, with bromocresol purple an even more acid exponent, 5.8. Colorimetric test of the distilled water which was used as a control, showed an exponent of 6.3 with bromocresol purple; with methyl red the color was a yellow which could not be used for measurement, as it lay outside the useful range. The experiment with litmus strips was similar to the one just described. At the end of one hour no changes could be seen in any of the papers when removed from solution and examined at once. After 2 hours a slight reddening was beginning to show in spots on both the neutral and the blue papers, in both the acid solution and the distilled water, the effect of the acid solution being but very slightly greater than the effect of the water. Now when blue and neutral litmus papers were dipped into the buffer mixtures it was found that not only the buffer mixture having a hydrogen-ion exponent of 5.8, *but even the buffer solution having the very much less intense acidity of 6.8 reddened the papers instantly*. The 6.8 buffer mixture did not appreciably affect the color of red litmus paper of the same make. The 7.0 (neutral) buffer mixture turned both red and blue papers instantly to an intermediate tint.

These experiments show that the speed with which litmus paper turns depends in very large measure on the buffer action of the solution under test, and one may easily be led to absolutely wrong conclusions as to the relative intensity of acidity in various solutions, soil extracts, or even moist soils, if this factor is left out of consideration. Unless special precautions are taken, litmus paper can not be used to arrange a group of soils according to their relative acid intensities.

The importance of the buffer factor is due to the fact that the litmus

[1] Prepared by dissolving methyl red in a slight excess of alkali and diluting.

[2] This means that the hydrogen-ion *concentration* was $1/10^{4.8}$. It is more convenient to use only the exponent, however, the exponent 7 indicating neutrality.

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paper has a certain acidity or alkalinity of its own which has to be changed by the action of appreciable quantities of alkali or acid before the paper can show the reaction of the fluid in which it is immersed. All indicators have this failing to some extent, but litmus, even in solution, is a poor indicator, and on paper it is even worse from this point of view.

The reason why moist soil turns litmus paper far more readily than does the soil extract is simple, and to harmonize its behavior with the presence of "true acidity" in soils does not require, as Harris suggests, that the hydrogen ions must be bound in a mysterious manner to the soil particles. The solubility of the acidic substances of most soils is very small. When litmus paper is dipped into a soil extract the reaction of the extract in the neighborhood of the paper is changed in overcoming the reaction of the litmus paper itself. If a small volume of extract is used, much of its acid substance may be thus used up; if a sufficiently large volume is used, time will be required for diffusion, a greater quantity of dye may leach from the paper, and a negative result still be obtained. When the litmus paper is brought into contact with the moist soil, the acid used up by the litmus paper is supplied again by the soil particles to the solution *near the litmus*, and the speed of the process may be infinitely greater.

There is therefore no ground for classifying soils into two types, "truly acid," and otherwise, by means of the behavior of litmus paper toward the soil extract and the moist soil, as was done by Harris in his more recent article.

The work of Walpole would lead us to suppose that many soil extracts thought to be neutral to litmus might in fact turn litmus paper if a good paper be used and exposed to a considerable volume of the extract for a sufficient length of time. He allowed in some cases 24 hours to elapse. However, in addition to the difficulties mentioned by him we have in many soil extracts, even after the use of a centrifuge, the further difficulty due to the obscuring effect of floating and suspended material. To filter the extracts through porcelain candles or even through paper before testing is of course inadmissable, unless it can be shown that the treatment does not change the reaction.

Soil chemists do not as yet generally realize the progress which has been made in the development of brilliant and reliable indicators. A careful treatment has recently been given by Clark and Lubs,[1] who themselves prepared new and useful indicators,[2] which we found useful in soil work. Paranitrophenol was discarded in this laboratory in the first preliminary experiments, though recently stated to be a splendid indicator by Christensen,[1] who wrote without knowledge of the newer indicators or

[1] *J. Bact.*, **2**, 1, 109, 191 (1917).
[2] *J. Wash. Acad. Sci.*, **5**, 609 (1915); **6**, 481 (1916).
[3] *Soil Science*, **4**, 115 (1917).

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of the application of them together with the hydrogen electrode to soil study.

The litmus paper test, as applied to moist soil, is simple, and with suitable precautions it can be made to yield information of some practical value. It is likely that some other indicator will eventually be found more useful. The choice of a simple test should await more definite information on the relation of hydrogen-ion concentration to the various biological activities of soil.

Summary and Conclusions.

The action of humus on solutions of sodium, potassium, and barium chlorides of different strengths was studied by means of the hydrogen electrode. The measurements showed that on the addition of chlorides to humus solutions or suspensions the potential of the gas chain was very considerably lowered, showing that there was a large increase of hydrogen-ion concentration.

Similar effects of smaller magnitude were seen in the action of potassium chloride on true solutions in the absence of humus or undissolved substance; these effects make it unsafe to draw conclusions as to the detailed mechanism of the process in the case of humus.

At equivalent concentrations barium chloride exerted the greatest effect on the potential of humus preparations. The direction of the diffusion potentials and the uncertainty of their magnitude would seem to make it unsafe to conclude from these experiments that barium reacts more extensively with humus than potassium.

Some experiments with litmus paper served to call attention to the difficulties and limitations of the litmus paper test as applied to soils and soil extracts. These experiments make it plain that there is no ground for a recent classification of soils which respond in the moist state to blue litmus paper into two types: "truly acid" and otherwise, according to the behavior of the litmus paper toward the aqueous soil extract.

Litmus paper can not be used, without suitable precautions, to arrange soils in the order of their intensities of acidity.

No proof has yet been brought forth that soils can act on litmus paper solely by virtue of their adsorptive capacity. The behavior of litmus paper toward the moist soil and the soil extract can be explained in a simple way without reference to adsorption.

It has been pointed out that it is dangerous to make broad general statements as to the cause of soil acidity.

Against the positive evidence, obtained by means of the hydrogen electrode and suitable indicators, in favor of the common occurrence of truly acid soils, there has been produced no valid negative evidence, based on adsorption or on the behavior of soils toward neutral salts. Truly acid

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soils are not rare, but very common and widely distributed in the United States.

[CONTRIBUTION FROM THE CARBOHYDRATE LABORATORY, BUREAU OF CHEMISTRY UNITED STATES DEPARTMENT OF AGRICULTURE.]

THE ROTATORY POWERS OF THE AMIDES OF ACTIVE α-HYDROXY ACIDS.

BY C. S. HUDSON.

Received February 13, 1918.

Weerman[1] has recently published measurements of the rotatory powers in water of the amides of seven monobasic acids of the sugar group. A comparison of the configurations that have been established for these acids or their amides by Fischer with their rotations is shown in the following table:

TABLE I.—CONFIGURATIONS AND SPECIFIC ROTATIONS.

Amide.	Fischer's configuration.	α-Carbon OH position.	Specific rotation.
d-Gluconic amide.....	H H OH H O CH_2OH . C . C . C . C . CNH_2 OH OH H OH	Below	+33.8°
d-Galactonic amide.....	H OH OH H O CH_2OH . C . C . C . C . CNH_2 OH H H OH	Below	+36.7°
l-Mannonic amide.....	OH OH H H O CH_2OH . C . C . C . C . CNH_2 H H OH OH	Below	+29.9°
d-Gulonic amide.....	H OH H H O CH_2OH . C . C . C . C . CNH_2 OH H OH OH	Below	+16.1°
l-Arabonic amide.....	OH OH H O CH_2OH . C . C . C . CNH_2 H H OH	Below	+38.4°
l-Ribonic amide.....	OH OH OH O CH_2OH . C . C . C . CNH_2 H H H	Above	−15.7°
d-Xylonic amide.....	H OH H O CH_2OH . C . C . C . CNH_2 OH H OH	Below	+44.5°

It will be seen that *the dextrorotary amides have the hydroxyl group below the asymmetric α-carbon atom, while the levorotary ones have it above.* Recently Dr. E. Yanovsky has measured for me the rotation of *d*-α-glucoheptonic amide, CH_2OH . C (H) . C (OH) . C (H) . C (H) . C (OH) . CNH_2, and Dr. L. H. Chernoff

[1] Dissertation "Over de Inwerking van Natriumhypochloriet op Amiden van Onverzadigde Zuren en Oxyzuren," published by A. H. Kruyt, Amsterdam, 1916.

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that of *l*-rhamnonic amide, $CH_3 . \overset{OH}{\underset{H}{C}} . \overset{OH}{\underset{H}{C}} . \overset{H}{\underset{OH}{C}} . \overset{H}{\underset{OH}{C}} . \overset{O}{CNH_2}$. Both substances were dextrorotary in agreement with the above relation. This relation is the same one that has been noted previously by Levene[1] for the direction of rotation of the salts and the phenylhydrazides of such acids. It is analogous to the relation that I have shown to hold between the direction of rotation and the position of the hydroxyl group on the γ-carbon atom of the lactones of these acids.[2] These rules for the direction of rotation may be easily remembered if the formulas are looked upon as placed vertically with the carboxyl group at the top, since a hydroxyl group on the right of the γ-carbon atom indicates that the lactone will rotate to the right and *vice versa*, and a hydroxyl on the right of the α-carbon indicates that the amide, the phenylhydrazide and the salts will rotate to the right. It is not surprising that the rotations of the amides are found to follow the same rule as do those of the phenylhydrazides because the latter compounds may be looked upon as substituted amides, $R.CHOH.CONH_2$ becoming $R.CHOH.CONH.NH(C_6H_5)$. Probably other substituted amides of these acids, such as the anilides $R\text{-}CHOH.CONH.C_6H_5$, follow the same rule.

It would be interesting to consider in a quantitative way the rotations of the amides that are mentioned in the table, but Weerman's actual readings are so small, in most cases less than two degrees, that the recorded specific rotations may be uncertain to the extent of several per cent. It seems possible, however, to draw at least one quantitative conclusion from them. By the same method of calculation that was used for the phenylhydrazides[3] the individual specific rotations of the 4 asymmetric carbon atoms of the hexonic amides may be found from the rotations of gluconic, mannonic, gulonic and galectonic amides to be, for the α-carbon $+32$, β-carbon -10, γ-carbon -1, and the δ-carbon -7. Although these values may be changed somewhat by more accurate measurements they clearly show that the α-carbon is so strongly rotatory in these compounds that its influence determines the direction of rotation for the whole structure.

The Rotatory Powers of Tartaric and Tartraminic Acids and Tartramide.—It has been shown by Fischer[4] that dextrorotary tartaric acid ($[\alpha]_D^{20} = +14°$ in 5% aqueous solution[5]) has the configuration

[1] *J. Biol. Chem.*, **23**, 145 (1915); Levene and Meyer, *Ibid.*, **26**, 355 (1916); **31**, 623 (1917). Regarding the phenylhydrazides, see also Hudson, THIS JOURNAL, **39**, 462 (1917).

[2] THIS JOURNAL, **31**, 338 (1910).

[3] *Ibid.*, **39**, 465 (1917).

[4] *Ber.*, **29**, 1377 (1896).

[5] Landolt, *Ibid.*, **6**, 1073 (1873).

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$$\begin{array}{l} \quad\;\; OH\;H \\ CHOH\,.\,C\,.\,C\,.\,COOH \\ \quad\;\; H\;\;OH \end{array}$$

, hence its mono-amide, tartraminic acid, must have the configuration

$$\begin{array}{l} \qquad\qquad\quad OH\;H \\ CONH_2\,.\,C\,.\,C\,.\,COOH \\ \qquad\qquad\quad H\;\;OH \end{array}$$

and its di-amide, tartramide, the structure

$$\begin{array}{l} \qquad\qquad\quad OH\;H \\ CONH_2\,.\,C\,.\,C\,.\,CONH_2 \\ \qquad\qquad\quad H\;\;OH \end{array}$$

. In the last formula the position of the hydroxyl group on each of the two α-carbons is to be considered as on the right, the carbon chain being written vertically and the two amide groups placed successively at the top. Both asymmetric carbon atoms, therefore, rotate to the right and it is to be expected that tartramide has a high dextrorotation; in agreement with this conclusion its specific rotation in water has been found by Frankland and Slator[1] to be +106.5. Walden[2] found the value 109°. Since the configuration of tartraminic acid may be regarded as consisting of half that of tartramide and half that of tartaric acid, the rotation of tartraminic acid may be expected to be the mean of +14 and +106.5 or +60°. In satisfactory agreement with this calculation Weerman[3] has found the value +64, and the last unit is uncertain because the actual reading that he observed was only about 4°. If Walden's value of 109 is used in the calculation the agreement is still better. Both tartramide and tartraminic acid, therefore, conform to the general relation for the direction of rotation of the amides.

The Configurations of the Active Malic Acids.—Naturally occurring malic acid is of levorotation in dilute aqueous solution. Its antipode has been produced by the reduction of natural (dextrorotary) tartaric acid[4] with hydriodic acid, hence Fischer has assigned to levorotatory malic acid the configuration

$$\begin{array}{l} \qquad\qquad\quad OH \\ COOH.CH_2\,.\,C\,.\,COOH \\ \qquad\qquad\quad H \end{array}$$

. The di-amide of this acid must accordingly be assigned the configuration

$$\begin{array}{l} \qquad\qquad\qquad\qquad OH \\ CONH_2.CH_2\,.\,C\,.\,CONH_2 \\ \qquad\qquad\qquad\qquad H \end{array}$$

. Since this formula contains only one asymmetric carbon atom and the hydroxyl group is on the left of this carbon, it is to be expected that the

[1] *J. Chem. Soc.*, **83**, 1354 (1903). Regarding the dextrorotation of a large number of substituted di-amides of dextro tartaric acid, which agree with the relation, see Frankland and Twiss, *J. Chem. Soc.*, **89**, 1853 (1906).

[2] *Z. physik. Chem.*, **17**, 707 (1895).

[3] Dissertation, p. 109.

[4] Bremer, *Ber.*, **8**, 861 (1875).

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di-amide of natural malic acid will be levorotary in case the above configuration is correct. Such is the fact, the specific rotation in water having been observed by Walden[1] to be —38°. This agreement is supported by Walden's further observation that the di-anilide, di-*o*-toluide, and di-*p*-toluide of natural malic acid are all strongly levorotary substances. A number of other substituted malamides that have been measured by Frankland and his pupils[2] also agree with the relation. This confirmation of the configuration of the active malic acids is of theoretical value just now because Freudenberg[3] has recently passed from active malic to active lactic and active glyceric acids, and has obtained the configurations of the latter two in terms of the configuration of malic acid. As Freudenberg remarks, however, the yield of active malic acid from the reduction of dextrorotary tartaric acid is only 2% which, of course, is so low that the selected configuration of malic acid is rendered doubtful. The present new proof, however, shows that the hitherto accepted configuration of Fischer's is correct and that the configurations which Freudenberg has assigned to lactic and glyceric acids are in consequence also correct. The configurations of active lactic, glyceric and α-hydroxy butyric acids could doubtless be obtained directly, without reference to syntheses from other substances if the rotations of the corresponding amides were known, which is not the case at present.[4]

The Configurations of the Active Mandelic Acids.—The mandelic acid which is obtained from amygdalin has a specific rotation[5] to the left, $[\alpha]_D^{22} = -153°$ in water and —148° in acetone. Its amide has been found by Walden to rotate to the left, $[\alpha]_D^{22} = -67$ in acetone and without doubt it would be strongly levorotary in water. The configurations of the active mandelic acids are accordingly considered to be

[1] *Z. physik. Chem.*, **17**, 249 (1895).

[2] McCrae, *J. Chem. Soc.*, **83**, 1324 (1903).

[3] *Ber.*, **47**, 2027 (1914).

[4] After sending in this article for publication I have fortunately found that Frankland, Wharton and Aston (*J. Chem. Soc.*, **79**, 266 (1901)) have measured the rotation of the amide of one of the active forms of glyceric acid. Their acid rotated to the right, its calcium salt rotated to the left and its amide rotated strongly to the left ($[\alpha]_D^{20} = -46°$ for the liquid amide without any solvent and $[\alpha]_D^{20} = -66°$ in methyl alcohol). There can hardly be any doubt that the amide would rotate to the left in water. Consequently dextrorotary glyceric acid is to be assigned the configuration

$$\begin{array}{c} COOH \\ \bullet \\ HOCH \\ \bullet \\ CH_2OH \end{array}$$

This confirms Freudenberg's proof for glyceric acid.

[5] Walden, *Z. physik. Chem.*, **17**, 706 (1895).

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COOH	COOH
•	•
HCOH	OHCH
•	•
C_6H_5	C_6H_5
Dextro-mandelic acid,	Levo-mandelic acid,
$[\alpha]_D^{20} = +153$.	$[\alpha]_D^{20} = -153$.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE SHEFFIELD LABORATORY OF PHYSIOLOGICAL CHEMISTRY, YALE UNIVERSITY.]

THE EDIBLE LITCHI NUT (Litchi Chinensis).

BY B. E. READ.

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The so-called Chinese hazel nut, *Litchi Chinensis* Sonner, (syn. *Nephelium litchi*, *Litchi* Sonn.), together with the allied species of the *Nephelium* occurs in the tropical countries of the far east where it is cultivated for medicinal and edible purposes. The litchi belongs to the genus *Alectryon* of the natural order *Sapindaceae*, which genus consists of more than 16 species, all of which are arborescent and are distributed over the Malayan, Papuan and Pacific Islands, being represented in the latter 2 groups by this particular species *Nephelium*. The type of this genus is the Titaki of New Zealand, *Alectryon excelsus*, which like the Hawaiian Mahoe has edible fruits.[1] It is singular that while the leaves and branches of many of these trees are unquestionably poisonous the fruit of others is valuable as an article of diet. The litchi nut and the longan and rambutan fruits as such are greatly appreciated for their excellent flavor and are used in "inflammatory and bilious fevers."

Of these many useful fruits only one, the litchi nut, has established itself through Chinese sources on the American market. There are said to be 8 varieties of this nut, which may account for varying reports about them. Those imported here from Canton are nearly globose with a dull brick-red pericarp which when ruptured exposes a sweet, brown, fleshy arillus surrounding a glossy chestnut-brown, orbicular seed, described in detail by Engler and Prantl.[2]

The litchi nut has long been used by the Chinese in medicine, the following paragraph from the Chinese Materia Medica giving a good idea of how highly it is esteemed by them.[3]

Nephelium Litchi.—Many of the sapindaceous plants are poisonous but the nephelium fruits are an exception, being much esteemed both in the fresh and dry

[1] J. F. Rock, "The Indigenous Trees of the Hawaiian Islands" (1913).

[2] Engler und Prantl, "Die Natürlichen Pflanzen-familien," Wilhelm Engelmann, Leipzig (1896).

[3] Stuart, G., "Chinese Materia Medica." Published by *Presbyterian Mission* Press, Shanghai (1911).

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state. Fukien Litchi is regarded as the best. The fruits are dried in the sun or by artificial heat, and are used as sweetmeat at feasts, and often given as presents to the newly married. They are not regarded as entirely without deleterious properties, and when the raw fruits are partaken of freely they are said to produce feverishness and nosebleed. Partaken of in small quantity or in the dried form they are thirst relieving and beneficial to nutrition. But they are specially recommended in all forms of gland enlargements and tumors. The seeds are regarded as anodyne and are prescribed in various neuralgic disorders and in orchitis. The leathery external tegument of the fruits is used in decoction in the distress caused by small-pox eruption, and also in fluxes from the bowels. The flowers, bark and root are employed in decoction in angina and quinsy.

It is furthermore cited by Hooker in "The Flora of British India," and by Kurz in "The Forest Flora of British Burma," the variety mentioned having a white edible arillus. In the latter country it is specially cultivated at Chittagong and has a local name "Kyet Mouk," though probably not indigenous there.

In view of the above facts and the present efforts toward food economy it was thought profitable to investigate the composition of these nuts, to obtain a correct estimate of their food value and moreover to look for the reason of their popularity as a drug in curing sickness.

Therapeutic Activity.—The diseases mentioned suggest the possible presence of iodides, alkaloids or a bitter substance of strong therapeutic action. The mention of feverishness and nosebleed produced when the nuts are freely partaken of, together with the fact that this plant is a member of the soapwort family would point to the presence of a saponin. No iodine was found present to account for its alleged action on tumors and gland enlargements, such as present-day treatment for goitre would suggest, and no saponin or similarly active substance was detected to account for its supposed toxicity. When added to the regular diet of a rabbit, for a long period or when fed in as large a quantity as 50 g. at one time, no toxic effects whatever from the nuts were observed.

These results confirm the opinion that statements regarding old native drugs may be very inexact and unreliable; which is not surprising when one remembers the empirical development of old Chinese medicine, its confused ideas about disease, and its lack of specific scientific facts concerning the name, natural order and habitat of any plant used.

Food Value.—The proximate composition of the litchi has been estimated by Atwater and Bryant.[1] Like the chestnut it is practically fat free, contains little, if any, protein, and consists very largely of "fiber and nitrogen free extract." The latter was found to be composed almost entirely of simple sugars, which accounts for the inclusion of these nuts as a food and for the claim that they are "beneficial to nutrition."

The various extracts prepared were acid, and showed the presence of

[1] U. S. Dept. Agr. Off. Exp. Sta., *Bull.* 28.

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citric acid with possible traces of the other common fruit acids, which stimulate the appetite and are well known as "thirst relieving substances." There was no pectin body present; but this fruit with its high sugar and acid content on the addition of orange fruit would form an excellent jelly suitable for nephritic and other limited diets, required for diminishing the acidity of the urine.[1]

It is reported by Street[2] that owing to its high carbohydrate content 7 g. of litchi are of equivalent calorific value to 10 g. of wheat bread. No other of the many fresh fruits or nuts cited by him show as high a value. I have found the carbohydrate to be a mixture of simple sugars chiefly invert sugar, a carbohydrate easily digested with all its energy available for use in the body.

Examination of the ash showed considerable content of the mineral salts needed in a well-balanced diet; thus the nut would make a good supplement to foods rich in protein and those lacking in mineral matter.

The many valuable suggestions of Langworthy[3] on the use of fruit as a food could be applied to the canning, preserving, drying, and general preparation of this fruit as a wholesome, palatable and attractive addition to the diet.

Experimental Part.

The proximate analysis corresponded with that given by Atwater and Bryant[4] as follows:

Ash, 1.5%; protein, 2.9%; ether extract, 0.2%; fiber and nitrogen-free extract, 77.5%; water, 17.9%.

I obtained very different values for the last 2 items; the amount of water might easily vary in a dried preparation like this.

2.1809 g. heated at 105° to constant weight lost 0.889 g. = 40.8%.

Preliminary Examination.—A preliminary qualitative examination was made of a simple aqueous extract prepared by rubbing up the fruit with water. The solution obtained had a strong reducing action on Fehling's solution, was levorotatory, fermented readily with yeast, yielded a small amount of a hydrazone when treated with phenylhydrazine in the cold for 24 hours. When heated with the same reagent for 10 minutes on the boiling water bath it formed a large amount of an osazone melting at 203°. A strong reaction was obtained with Seliwanoff's test for levulose. Biuret and various other protein tests gave negative results with the water extract. Hot water extracts showed no visible reaction with iodine or iron salts, indicating the absence of starch or tannin.

Five fruits weighing approximately 13 g. were thoroughly extracted with

[1] Editorial, *J. Am. Med. Assoc.*, **69**, 1433 (1917).
[2] Street, J. P., "Diabetic Foods," *Conn. Agr. Exp. Sta.*, p. 93 (1913).
[3] U. S. Dept. Agr., *Farmer's Bull.* 293 (1917).
[4] *Loc. cit.*

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cold water. The clear solution obtained after filtering off a small amount of insoluble fiber was diluted to 1000 cc. and the rotatory and reducing power estimated. There was no increase in either value after hydrolysis of the solution with acid, thus showing the absence of complex sugars.

25 cc. of the solution gave by Allihn's method 0.3834 g. CuO. For pure invert sugar this is equivalent to 664 mg. per 100 cc., or 51.1% of the original substance.

The solution placed in a 2 dcm. tube gave a rotation of —0.95 V°. This reading is a little too high for 51% of invert sugar and indicates the presence of traces of other levorotatory substances.

A detailed scheme of analysis was made based chiefly on that outlined by Street and Bailey.[1] Successive alcoholic, aqueous, acid and alkaline extracts were prepared for examination of their carbohydrate content and estimation by Allihn's copper method. Other less significant data were obtained relating to acid content, crude fiber, etc.

Alcoholic Extract.—100 g. of the edible portion were finely divided and heated with 1000 cc. of 95% alcohol on a boiling water bath for 8 hours. Nearly all of the fruit dissolved. After standing 24 hours, the small insoluble portion, weighing 8.0 g. when dried, was filtered off.

The alcoholic extract was evaporated nearly to dryness on a boiling water bath, and taken up in 1000 cc. of water. The solution obtained was treated with lead acetate in the usual way, and the clear filtrate after dilution with 7 volumes of water used to determine reduction and polarization values. The values obtained corresponded with those of the preliminary aqueous extract; hydrolysis with acid also made no change.

Portions of 25 cc. of the solution yielded 0.3784 g. CuO. This is approximately the amount of CuO obtainable if all the soluble material were invert sugar. It is equivalent to 52.9% invert sugar.

Aqueous Extract.—The dried residue from the alcoholic extraction was further extracted with 400 cc. of cold water for 48 hours. The dark-colored solution obtained was filtered off and treated with lead acetate which cleared and almost decolorized it. The solution showed no rotation or reduction of copper solution, the sugars having all been withdrawn in the alcoholic extract.

Acid Extract.—The residue was treated with 250 cc. of 1% hydrochloric acid for 6 hours on a boiling water bath to extract the hemicelluloses. Aliquot parts equivalent to 20 g. of litchi yielded 0.045 g. CuO by Allihn's method. This is equivalent to 0.1% glucose-yielding substance in the original fruit.

Alkali Extract.—The small amount of remaining insoluble material was boiled with 200 cc. of 1% caustic soda for 45 minutes and filtered. The extract when neutralized gave a heavy brown precipitate of humin sub-

[1] Street, J. P., and Bailey, E. M., *J. Ind. Eng. Chem.*, 7, 853 (1915).

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stance which contained no easily hydrolyzable carbohydrate. The dried insoluble portion represented 0.4% "crude fiber."

Organic Acids.—The heavy flocculent lead precipitate from the alcoholic extract was treated with hydrogen sulfide, and after removal of the lead sulfide and excess of hydrogen sulfide, was tested by the usual methods for a saponin body.[1] None was detected. The solution was acid. Citric acid had been identified by preliminary examination. The calcium precipitate obtained on the addition of calcium chloride was insoluble in either acetic acid or caustic soda, and the gelatinous precipitate obtained with barium hydroxide was insoluble in either dilute acetic acid or alcohol. Tests for malic and succinic acids showed negative results.

The free acid solution was titrated with decinormal alkali using phenolphthalein as indicator, and gave a mean of 19.2 cc. of alkali required to neutralize the acid from 50 g. of litchi, which is equivalent to 0.25% citric acid. The neutralized solution was then precipitated with barium chloride, the barium salt filtered off, dissolved in hydrochloric acid and the barium estimated as sulfate. The acid from 50 g. of litchi yielded 136 mg. of barium sulfate, which is equivalent to 0.21% of organic acid calculated as citric acid.

The small lead precipitate from the aqueous extract was treated in the same manner and yielded 85 mg. of $BaSO_4$, equivalent to 0.05% citric acid.

Acid- and Base-Forming Elements.—These were examined qualitatively by the methods of Sherman and Gettler.[2] Considerable amounts of calcium, magnesium, and iron were noted, and sulfate and phosphate ions were present in marked amount. No iodine was found when examined for by Hunter's method.

Glycogenetic Properties.—To confirm the results as to the nutritive value of the carbohydrate in the litchi, feeding experiments were conducted with rabbits according to the procedure carried out by Nakaseko[3] with inulin. After a 6-day fast 50 g. of litchi were fed and the animal killed within 16 hours. The liver was removed and the glycogen in it estimated by Pflüger's method with subsequent Allihn copper determinations.

Initial body weight	2040 g.
Final body weight	1820 g.
Duration of fast	6 days
Killed on the 7th day	..
Weight of liver	55.0 g.
Total glycogen found	5.86 g.
Glycogen in liver	10.7%

A control experiment was done, with a rabbit weighing 1900 g., which

[1] Haas, P., and Hill, T. G., "Chemistry of Plant Products," Longmans, Green & Co., London (1917).

[2] Sherman, H. C., and Gettler, A. O., *J. Biol. Chem.*, 11, 323 (1912).

[3] Nakaseko, R., *Am. J. Physiol.*, 4, 246 (1901).

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after a 6-day fast weighed 1600 g. The animal was killed and no glycogen whatever was found in the liver.

These results show in a most marked way the glycogenetic properties of the carbohydrates in the litchi nut.

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE COMMERCIAL RESEARCH COMPANY, NEW YORK, AND THE MELLON INSTITUTE, PITTSBURGH.]

THE ACTION OF CONCENTRATED SULFURIC ACID ON OLEFINS, WITH PARTICULAR REFERENCE TO THE REFINING OF PETROLEUM DISTILLATES.

BY BENJAMIN T. BROOKS AND IRWIN HUMPHREY.

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The original object of the investigation discussed in the following paper was to throw some light on the reactions involved in the refining of petroleum distillates, as ordinarily carried out in petroleum refineries. We were at first somewhat handicapped by the fact that previous work on the behavior of the olefins to conc. sulfuric acid was practically limited to the first 4 members of the series, ethylene, propylene, butylene and the amylenes. The present contribution, we feel, does little more than open up the subject. However, certain facts seem amply demonstrated, and some of these facts vary widely from those to be expected from the commonly accepted theories.

The recent extensive development of cracking processes for the manufacture of light petroleum distillates from heavier oils has emphasized the desirability of studying the reactions involved in refining such light oils. Petroleum distillates have been refined almost exclusively by treating with conc. sulfuric acid since the very beginning of the petroleum industry; in fact Benjamin Silliman advocated such a procedure in his famous report made in 1855. The industry has apparently been quite content to accept the results of this operation, inasmuch as products so refined are generally acceptable to the users and no better refining method has, up to date, found general acceptance.

Although the action of dil. sulfuric acid, about 5% by volume, on a few olefins of the terpene series has been studied, a general investigation of the action of this, or other mineral acids on olefines has never been made; particularly is this true of the concentrated acids. The theory which has found practically universal acceptance in the petroleum industry is that the olefins occurring in petroleum distillates are polymerized by the acid to *tars*, form so-called "sulfo acids," and are completely removed from the oils so refined. That *this assumption is wrong* and that the so-called quantitative method of removing olefins by sulfuric acid gives misleading results will be brought out in the following

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pages.[1] Indeed, Nef[2] claimed that *butylene* and the higher olefin homologs were quantitatively converted into polymers by strong sulfuric acid at 0°, while propylene remained dissolved in the acid as propyl sulfuric acid, and employed a quantitative method of separation of mixtures of these simpler substances, which was based on this idea. On the other hand, Wischnegradsky[3] claimed to have obtained large yields of fusel oil by the action of cold conc. sulfuric acid on "amylene" and isolated the alcohol by diluting the acid layer with water, thus precipitating an oil consisting, in part, of an amyl alcohol. In view of the general confusion of ideas on the subject, and the lack of definite data on the behavior of olefins of different constitutions to conc. sulfuric acid, it has seemed necessary to attack the problem along broad lines, and, instead of first attempting an analytical study of the "acid oils" obtained in refinery practice, we first investigated the behavior of synthetic unsaturated hydrocarbons of definite purity and known constitution.

Since the more theoretical phases of the question are inextricably bound up with the practical side, it has seemed necessary to embody the whole of our findings and the discussion of them in a single paper.

Theoretical Considerations.

The Principal Results of the Action of Sulfuric Acid on Olefins are Polymerization, the Formation of Secondary and Tertiary Alcohols and Mono- and Dialkyl Esters of Sulfuric Acid. None of the Simple or Mono-olefins Studied Yield Tars with Conc. Sulfuric Acids at 15°.—We find that the relative importance of the above noted effects varies widely and depends primarily upon the constitution and molecular weight of the various substances, the concentration of the acid, and time. We are able to confirm the surmise of Michael and Brunel[4] that in the aliphatic hydrocarbon series the tendency to form alkyl sulfuric esters and alcohols decreases with increasing molecular weight, this result appearing to be *maximum* with the amylenes and hexenes.

Michael and Brunel showed that isobutene $(CH_3)_2C = CH_2$ is rapidly and completely dissolved by sulfuric acid, 63% H_2SO_4, at 17°. Also, tetramethyl ethylene $(CH_3)_2C = C(CH_3)_2$ reacts readily and completely with 77% acid at ordinary temperatures, but not as rapidly as the amylene $(CH_3)_2C = C\begin{smallmatrix}H\\CH_3\end{smallmatrix}$. Of the 2 amylenes $\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}\!\!>\!CHCH = CH_2$ and

[1] It should be pointed out that in the original method for determining olefins, which was proposed by Krämer and Böttcher, fuming sulfuric acid was stipulated, but Worstall (*Am. Chem. J.*, 20, 664 (1898)), has pointed out, and it is a matter of common experience, that fuming sulfuric acid will attack saturated hydrocarbons.

[2] *Ann.*, 318, 26 (1901).

[3] *Ibid.*, 190, 328 (1877).

[4] *Am. Chem. J.*, 41, 118 (1909).

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$\begin{matrix} C_2H_5 \\ CH_3 \end{matrix}\!\!>C = CH_2$, the latter dissolves more readily in 66% acid. Michael and Brunel did not differentiate between the formation of *alcohols* and *sulfuric esters*, nor between unchanged hydrocarbons and polymers, but speak only of the hydrocarbons going into solution. In this connection it should be pointed out that with relatively dilute acids practically complete hydration to alcohols can occur without noticeable absorption, as in the commercial process for the manufacture of terpineol. Results very closely parallel to these have been noted by others in the case of the additive power of the amylenes and the halogen acids.[1]

As regards the *effect of the constitution* of the olefins on their reactivity to sulfuric acid, the following can be said: The substitution for the hydrogen of ethylene groups, which impart a strongly electronegative character, results in decreased reactivity to sulfuric acid. Thus we find that cinnamic and fumaric acids are not appreciably acted upon by 95% sulfuric acid at ordinary temperatures; and similarly dichloroethylene is acted upon only very slowly under the same conditions. Allyl bromide is also more stable toward conc. sulfuric acid than is propylene.[2] On the other hand we find that tetramethylethylene is more reactive toward the acid than is its isomer, α-hexene, which finds an explanation in the fact that the unsaturated group $>C = C<$ in α-hexene has 3 of its valences taken up by hydrogen, while in tetramethylethylene these are replaced by the more strongly electropositive methyl groups. From this standpoint the greater reactivity of amylene, butylene and propylene as compared with ethylene is also readily explained. The behavior of the olefins of still greater molecular weight, however, is difficult to explain. Why they should be quite stable, as compared with the amylenes and hexenes, is not apparent, nor has any explanation suggested itself to us as to why γ-ethyl-β-pentene should yield 72% alcohol and 12% polymers and α-methyl-β-undecene give 97% polymers and only a trace of alcohol, since their structures are quite similar.

$$\begin{matrix} CH_3 \\ H \end{matrix}\!\!>C = C\!<\!\!\begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix} \qquad \begin{matrix} C_8H_{17} \\ H \end{matrix}\!\!>C = C\!<\!\!\begin{matrix} CH_3 \\ CH_3 \end{matrix}$$

In the same way the known differences in the behavior of vinyl acetic acid $H_2C = CH.CH_2CO_2H$ and its isomer $H_2C = C\!<\!\!\begin{matrix} CH_3 \\ CO_2H \end{matrix}$ are difficult to explain. With 5% sulfuric acid, the former yields solid crotonic acid while the latter gives a polymerization product.

[1] Butlerow, *Ann.*, **189**, 51 (1877); *Ber.*, **12**, 1483 (1879); Wischnegradsky, *Ibid.*, **190**, 351 (1878); Eltekow, *Ibid.*, **10**, 707 (1877); Konowalow, *Ibid.*, **13**, 2395 (1880).

[2] Cf. Michael, *Ber.*, **39**, 2785 (1906).

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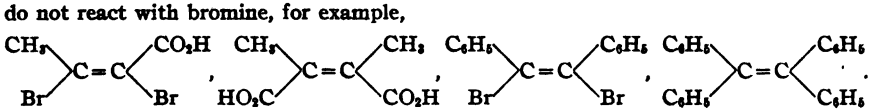
The tendency of the olefins and substituted ethylenes to react with sulfuric acid is distinctly less than their tendency to combine directly with bromine. Thus, cinnamic and fumaric acids, mentioned above, both readily yield dibromides, as is well known.[1]

Styrene, cinnamic alcohol, cinnamic aldehyde, eugenol, isoeugenol and safrol are very energetically polymerized by 85% sulfuric acid at 0°. The polymers in these cases were hard resins and no other products were isolated. Allyl alcohol reacts energetically with 60% acid to form the ordinary allyl hydrogen sulfate, the ethylene group not being affected to any appreciable extent.

With Increasing Molecular Weight, the Tendency is toward Polymerization.—Thus, the duodecene studied gave the dipolymer almost quantitatively. We have observed no instance of ring formation. In other words, when polymerization occurs through the influence of the acid, the polymer or polymers still contain at least one double bond and these unsaturated hydrocarbons of high molecular weight, *i. e.*, *the polymers, are much more stable toward sulfuric acid than the parent olefins.* This is contrary to the popular idea, although this behavior is closely parallel to the observation of Kondakow,[2] who studied the addition of hydrogen chloride to isobutene and its polymers. This relatively greater stability of the polymers toward sulfuric acid has the result that *the more viscous heavier polymers are found not in the acid sludge, but, to a large degree, in the oil layer*, or the refined oils of the petroleum refiner.

It has generally been assumed that the viscous petroleum oils, of the lubricating oil type, consist exclusively of naphthenes and polynaphthenes. The analyses of such oils, freed from paraffin, indicate the empirical formulas C_nH_{2n} and C_nH_{2n-2}, and since they have undergone at least one treatment with sulfuric acid, such an assumption would seem superficially plausible. But, as we have shown, olefin hydrocarbons of large molecular weight are also viscous oils and are quite stable toward ordinary conc. sulfuric acid. The dipolymer $C_{24}H_{48}$ with one double bond of the duodecene mentioned above has a viscosity equal to light machine oil and the polymers of the unsaturated hydrocarbons prepared from cetyl alcohol and myricyl alcohol are quite viscous oils, very nearly identical in their common physical properties with lubricating oils of corresponding molecular weight. That unsaturated hydrocarbons have considerably

[1] Bauer and Moser, *Ber.*, **37**, 3317 (1904), have called attention to the fact that certain ethylene derivatives which contain strongly electronegative substituent groups do not react with bromine, for example,



[2] *J. prakt. Chem.*, [2] **54**, 449 (1896).

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higher viscosities than the corresponding saturated hydrocarbons, has been shown by Dunstan and Hilditch.[1]

That the *iodine numbers of refined lubricating oils indicate relatively very large percentages of unsaturated hydrocarbons* has been generally ignored. An iodine number of 12, in the case of a medium heavy lubricating oil, corresponds roughly to a mono-olefin content of 20%. The idea that the iodine numbers can be so interpreted has usually been rejected, evidently owing to the prevailing opinion that olefins of large molecular weight are, like turpentine, energetically polymerized to tars. Since we have found that the higher open-chain olefin hydrocarbons and their polymers, are relatively stable toward sulfuric acid, we are of the opinion that *the iodine numbers of some refined lubricating oils really indicate relatively large percentages of unsaturated hydrocarbons in such oils.*[2]

Theory of the Addition of Water to Olefins by Dilute and Concentrated Acids.

It has heretofore been supposed, and for good reasons, that when an alcohol is formed by the action of sulfuric acid upon an olefin that an ester of sulfuric acid is first formed, which is then hydrolyzed by water after the manner of the hydrolysis of ethyl hydrogen sulfate. Although these sulfuric acid esters can be hydrolyzed, as by boiling with water, we find abundant evidence that *alcohols are formed* at low temperatures, in the presence of sulfuric acid, *without the intermediate formation of sulfuric esters of the known type.* Thus, when the simpler alkenes, such as the amylenes, hexenes, or heptenes, are carefully treated with 85% sulfuric acid at temperatures not above 15° and the resulting *clear, amber-colored* acid solution is slowly added to shaved ice, there is immediately precipitated a pale yellow oil containing, as its chief constituent, the free alcohol corresponding to the original hydrocarbon. This does not increase in amount when the aqueous acid solution is permitted to stand at room temperature several days, although ordinarily 30 to 40% of the original hydrocarbon remains in solution as the acid sulfuric ester. In a number of these experiments the aqueous solution, separated from the alcohol layer, was thoroughly extracted with ether to remove traces of dissolved alcohol, and the dilute aqueous sulfuric ester solution slowly heated in an oil bath until the strong characteristic odor of these alcohols was perceptible. These experiments proved conclusively that the mono or acid esters of the amylenes, hexenes and heptenes are not appreciably hydrolyzed in 10 minutes at any temperature below 90°. This is also in accord with our observation that aqueous solutions of the barium salts

[1] *Z. Elektrochem.*, 17, 922 (1911).

[2] It should be pointed out that the iodine or bromine absorption values of oils are reduced by polymerization, a dipolymer of a simple mono-olefin having one-half the iodine or bromine absorption number of the original olefin.

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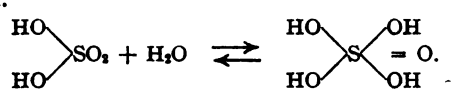
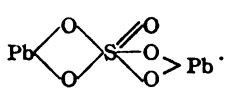
of these acid esters can be gently evaporated at about 40° without decomposition. The only measurements of the rate of hydrolysis of such esters which have been made appear to be those of Linhart,[1] who showed that a dilute solution of ethyl sodium sulfate was 16% hydrolyzed in 8 days at 60°.

On treating a mixture of hexenes with 100% sulfuric acid or with pure benzene sulfonic acid, no alcohols are formed. Also in comparative experiments, larger yields of alcohol were obtained with 85% than with 94% sulfuric acid. In other words, the water which is present in the reaction mixture, not the water in the subsequently diluted solution, enters into the reaction.

To account for the fact just mentioned, two theories have occurred to us which may lead to further information along these lines. One was suggested by the fact that the water in relatively concentrated sulfuric acid solutions is not present as such, but is combined, forming one or more of the well-known series of so-called hydrates. The best known perhaps is the monohydrate, the structure of which is probably that of orthosulfuric acid.



It is certain that esters of these 2 acids would have quite different degrees of stability and quite different rates of hydrolysis. All that can be said with certainty is that the ordinary esters $\begin{array}{c} RCH_2 \\ | \\ R_1CHOSO_3H \end{array}$ are relatively quite stable in aqueous solution. The orthosulfuric esters have not been isolated as such, but certain of the basic sulfates have been regarded as derived from it, as



This theory readily explains the fact that the alcohol is not present as such before diluting with water. The free alcohol, if present, should dissolve in an immiscible solvent such as chloroform, which, we find, is not the case.

We have also sought an explanation of the observed facts in the somewhat close analogies between the behavior of olefins toward conc. sulfuric acid and toward zinc chloride. Anhydrous zinc and aluminum chlorides form well characterized addition products with unsaturated hydrocarbons.[2] The compounds with zinc chloride react with water to

[1] *Am. J. Sci.*, **35**, 283 (1913).

[2] Kondakow, *J. prakt. Chem.*, [2] **48**, 472 (1893); [2] **54**, 447, 454 (1896); Henderson, THIS JOURNAL, **38**, 1382 (1916); Gangloff and Henderson, *Ibid.*, **39**, 1420 (1917).

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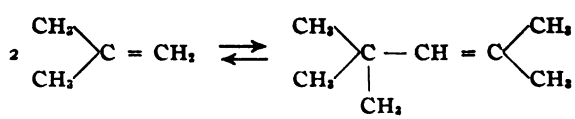
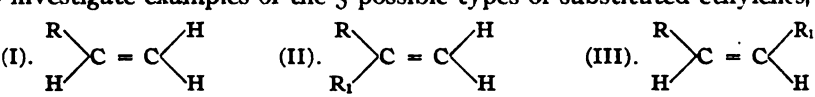
give, in part, alcohols. The analogy is made more complete by the fact that the oil precipitated by pouring an apparently clear sulfuric acid-olefin solution into water or cracked ice, often contains a considerable proportion of the original olefin, or one of its isomers.[1] It should be pointed out, however, that the isolation of the so-called addition compounds with zinc chloride and aluminum chloride, likewise the well-known mercury ethanol compounds, is particularly easy, well-defined crystalline compounds being formed. With the sulfuric acid solutions, in contrast, we have been unable to isolate any such addition product. The cryoscopic method so successfully employed by Kendall is not applicable in this case. We endeavored to get indirect evidence in this manner by selecting a crystalline acid which has marked reactivity toward olefins, but little polymerizing action, *i. e.*, trichloroacetic acid, and the solid olefin hydrocarbon camphene. However, freezing-point curves of mixtures of these two substances gave no indication of the formation of an addition product.

Closely connected with the alcohol formation is the mechanism of the polymerization. Previous work throws practically no light on this phase of the subject. Certainly from what is known, no generalizations can be drawn. The only case where the constitution of the zinc chloride or sulfuric acid polymer has been studied is that of isobutene and its dipolymer,[2]



The work of Harries on the ozonide degradation products of catalytically polymerized isoprene, or "isoprene rubber," indicates that in this case combination occurs exclusively through the α-carbon atoms of the groups $RCH = CH_2$. We have nothing to add to the theory of polymerization by means of sulfuric acid except the observation that the polymers, in the cases studied by us, contain one double bond. In other words, ring formation with the mono-olefins has not been observed to occur.

The preparation of unsaturated hydrocarbons of definite constitution and free from isomers presented a little difficulty, inasmuch as we desired to investigate examples of the 5 possible types of substituted ethylenes,



[1] Examples of isomerization by means of sulfuric acid are fairly numerous; for example $(CH_3)_2CH.CH = CH_2$ to $(CH_3)_2C = C\langle^{CH_3}_{H}$, isopulegone to pulegone, alpha pinene to terpinene, etc.

[2] Kondakow, *Loc. cit.*

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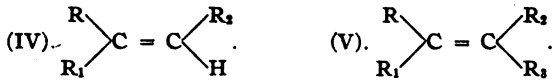
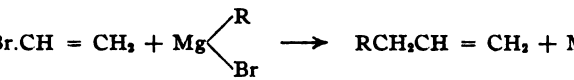


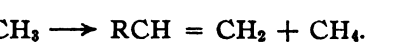
In several instances this was accomplished by removal of water from alcohols or hydriodic acid from alkyl iodides having certain symmetrical structures, for instance the alcohol triethyl carbinol and the iodide $CH_3CH_2CH_2CHI.CH_2CH_2CH_3$.

The normal α-olefins were prepared by a simple adaptation of the synthesis of allyl derivatives of benzol, which has been described by Tiffeneau.[1] We find that allyl bromide reacts smoothly with the magnesium alkyl bromides to give α-olefins.[2]



In view of the fact that some of the α-olefins prepared in this way possess physical properties differing considerably from the properties attributed to these hydrocarbons in the literature we have reviewed the older methods of preparing them and conclude that the present instance is the first time certain of these substances have been isolated in a pure state.

Hydrocarbons of this type seemed to be of considerable importance in connection with the behavior of the unsaturated petroleum oils since Brochet[3] claimed to have identified α-hexene and α-pentene in the light distillate from bog head coal, and Haber[4] has claimed that paraffin hydrocarbons dissociate under the influence of heat, mainly to give methane and an α-olefin, as in the reaction



Thus Haber showed that between 600° and 800° hexane decomposed mainly to methane and an amylene and wrote the above equation to express this change, although he did not examine the structure of the resulting amylene. In view of the well-known tendency of α-olefins to rearrange,[5] we regard the assumption that the unsaturated hydro-

[1] *Compt. rend.*, **139**, 481 (1904).

[2] Although this reaction proceeds very smoothly, we have noted that magnesium allyl bromide reacts with the alkyl bromides, as propyl bromide, only very slowly, the yields of hydrocarbon being very poor.

[3] *Bull. soc. chim. phys.*, [3] **7**, 566 (1892).

[4] *Ber.*, **29**, 2691 (1896).

[5] The rearrangement of methylbutene $(CH_3)_2CHCH = CH_2$ to trimethylethylene $(CH_3)_2C = CH.CH_3$ is well established. Also Wurtz (*Ann.*, **127**, 55 (1863); **148**, 131 (1868)) attempted to prepare α-olefins by reacting upon the zinc alkyls with allyl

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carbons of cracked petroleum oils are of this type, to be entirely unwarranted and extremely improbable.

We have also employed the bromo-ester condensation method of Reformatsky and Wallach, as, for example the synthesis of α-octene from oenanthol, but this has proven of little value as a preparative method in the present instance since the unsaturated acids do not readily lose carbon dioxide.

As regards the formation of unsaturated hydrocarbons by decomposing secondary and tertiary alcohols, we have found that distillation of the alcohol to which a trace of iodine has been added gives very much better yields in many instances than the older methods. Thus triethylcarbinol readily yields the hydrocarbon $(C_2H_5)_2C = CHCH_3$ and the tertiary alcohol $CH_3(CH_2)_8C.OH(CH_3)_2$ gives a good yield of the hydrocarbon $CH_3(CH_2)_7CH = C\begin{smallmatrix}\diagup CH_3\\ \diagdown CH_3\end{smallmatrix}$, the constitution of which we were able to confirm by the formation of acetone by oxidation.

In view of the old process of manufacturing hydroxystearic acid from oleic acid by treating with conc. sulfuric acid in the cold, followed by steam hydrolysis, we thought that perhaps the higher straight-chain olefins of the type $\begin{smallmatrix}R\diagdown\\ H\diagup\end{smallmatrix}C = C\begin{smallmatrix}\diagup R_1\\ \diagdown H\end{smallmatrix}$ could be converted into wax-like alcohols, but the unsaturated hydrocarbons prepared from cetyl and myricyl alcohols react normally, that is, like other unsaturated hydrocarbons of 10 or more carbon atoms, giving polymers and small percentages only of soluble sulfuric esters. No trace of solid substance could be separated from the products by freezing. Nevertheless, we consider the preparation of solid waxes from the higher boiling unsaturated hydrocarbons of petroleum to be a possibility.

We find that saturated aqueous solutions of sulfur dioxide are entirely without action on the simple olefins at ordinary temperature. After 80 hours' shaking a petroleum hexene mixture with saturated aqueous sulfur dioxide the olefin was quantitatively recovered unchanged. Diolefins are known to give resinous polymers which contain sulfur.

Experimental.

β-Methyl-α-butane, $C_2H_5C\begin{smallmatrix}\diagup CH_3\\ \diagdown CH_2\end{smallmatrix}$.—A small amount of this amylene, boiling point 33–35°, made by decomposition with removal of water from

iodide, but when zinc ethyl is treated with allyl iodide, only β-pentene is obtained. The success of our method with the magnesium alkyl bromides is readily explained by the fact that the magnesium halides are not nearly so reactive toward olefins as are the zinc halides.

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dimethylethyl carbinol, dissolved completely in 2 volumes of 85% sulfuric acid in a few minutes at 10°. A yield of 45% of the theory of the original tertiary alcohol was liberated by diluting with ice water. No polymers were formed.

β-Methyl-α-pentene, $\begin{matrix} C_3H_7 \\ CH_3 \end{matrix}\!\!>\!C = CH_2$. — This hydrocarbon, boiling point 64–66°, was prepared by the action of bromoacetic ester and zinc on methylpropyl ketone and decomposition of the resulting oxy-ester and acid.[1] Since the hydrocarbon is evidently new, we regret that the small quantity of it available and the limited time at our disposal prevented us confirming the constitution inferred from the method employed in its preparation. The methylpropyl ketone used was isolated from acetone oil by repeated fractional distillation. The condensation with the ester proceeds smoothly, giving nearly theoretical yields of the oxyester, but on saponifying this ester with sodium methylate in methyl alcohol almost complete hydrolysis occurs, probably after the manner indicated by Wallach for other similar esters, to give the original ketone. From 200 g. of the ketone there was finally isolated only 12 g. of the hexene. From this small quantity of the olefin only part of the desired data was obtained. On treating at 10° with 2 volumes of 85% sulfuric acid the oil lost 55% of its volume by solution. On diluting with ice water 4.5 g. of light yellow oil were obtained, having the strong camphor-like odor common to the tertiary alcohols, indicating the presence of the alcohol $C_3H_7C.OH(CH_3)_2$.

Petroleum Hexene Mixture.—The material used in this experiment was a mixture of the olefins resulting from the action of alcoholic potassium hydroxide on monochlorohexanes and had a boiling-point range of 55–63°; specific gravity, 0.7045. To 200 g. of the hydrocarbon, 1.25 moles of sulfuric acid, sp. gr. 1.84, were added with cooling, the temperature being permitted to rise to 40°. The usual amber-colored viscous solution was formed. After standing half an hour the mixture was treated in the usual manner. The washed, supernatant oil, light yellow in color, measured 152 cc., sp. gr. 0.770, weight 117 g. Refluxing with aniline for 3 hours, according to the method of Heusler,[2] yielded aniline sulfate, determined in the aqueous washings as barium sulfate, equivalent

[1] We find that the condensation of methylpropyl ketone and bromoacetic ester in presence of zinc goes almost violently if the reaction materials are *thoroughly dried.* From 212 g. methylpropyl ketone we obtained 356 g. of the β-oxy-β-methylpentane-α-carbonic acid ethylester, a thick, viscous syrup, first described by Semlianizin (*J. prakt. Chem.*, [2] 23, 267 (1881)). But very poor yields were obtained on saponifying with sodium methylate in methyl alcohol. This fact and the cost of the materials required render the Reformatsky synthesis of little practical value as a preparative method.

[2] *Ber.*, 28, 488, 498 (1895).

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to 0.55 g. of sulfuric acid, but the decomposition of the sulfuric esters was incomplete, as shown by the evolution of sulfur dioxide when the oil was distilled.

Three fractional distillations of the oil readily resolved it into the following:

		B. p.	%.	Sp. gr.
I.	Unchanged hydrocarbon	60– 75°	21.0	...
II.	Intermediate fraction	75–190°	6.0	0.764
III.	Dipolymer	190–200°	35.0	0.784
IV.	Residue, higher polymers above	200°	36.0	0.836
	Loss	....	3.0	...

The dipolymer was unsaturated to cold dilute potassium permanganate and bromine in acetic acid.

The acid layer on diluting yielded 58.0 g. of oil, sp. gr. 0.872. This was distilled with steam until the camphor-like odor had disappeared, yielding 24 g. of oil, sp. gr. 0.827, 80% of which boiled at 130–140°, indicating a hexyl alcohol. Phenylisocyanate gave a phenylurethane melting at 235°. The aqueous acid layer was treated with barium carbonate and, on very gentle evaporation of the filtrate, the barium hexyl sulfate was obtained as a very soluble, somewhat gummy crystalline salt. After washing with a little alcohol, the salt analyzed as follows:

Calc. for $(C_6H_{13}OSO_3)_2Ba$: Ba, 27.8. Found: 28.1

Another quantity of hexene, made from crude monochlorohexane,[1] was treated successively with 85% and 95% sulfuric acid, the results indicating the increasing stability of the polymers to the acid. On treating 280 g. of the hexene, sp. gr. 0.7045, b. p. 55–63°, with 400 g. 85% of sulfuric acid, we recovered 164 g. oil, or 58.6% of the original oil. From the mixture of polymers we isolated by distilling at 26 mm. pressure 2 fractions, 100–150°, 57 g., sp. gr. 0.8180; and 150–190°, 51 g., sp. gr. 0.8442. These fractions were then treated with equal volumes of more concentrated acid, sp. gr. 1.84. The loss to the stronger acid was 31% for the lower boiling and 28% for the higher boiling fraction. Redistilling at 26 mm. showed that only 14% had been converted into still more complex polymers boiling above 190° at this pressure.

α-Hexene.—As noted in the first part of this paper, the majority of the normal α-olefins as described in the literature are in reality isomers of the olefins, or mixtures. Thus α-hexene is usually described as boiling at 68–70° and its history is readily traced to the early work of Morgan[2] and Schlorlemmer, who prepared the hydrocarbon by removal of hydro-

[1] We attempted to prepare the hexyl iodides from the chlorides by means of the well-known reaction with sodium iodide in acetone, but with very poor results. At ordinary temperatures very little reaction results and on warming abundant separation of iodine occurs.

[2] *Ann.*, 177, 305 (1875).

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chloric acid from a chlorinated hexane fraction, the latter having been obtained from petroleum. A close examination of Morgan's work indicates that his hydrocarbon was probably β-hexene. Zelinsky and Przewalsky[1] *heated* *n*-hexyl iodide with quinoline and obtained a liquid mixture boiling from 35° to 67°. On oxidizing the fraction boiling from 63.5–65° they obtained a mixture of butyric and valeric acids, showing that the hexene was a mixture of the α- and β-isomers. That α-olefins, if originally formed in a pyrogenetic process, tend to rearrange is indicated also by the formation of a hexene, probably β-, from normal heptyl alcohol by passing over finely divided nickel at 220°. The hydrocarbon so obtained boiled at 67.7–68.1° and was regarded by Van Beresteyn[2] as α hexene, expressing its formation as follows:

$$CH_3(CH_2)_3CH_2CH_2CH_2OH. \longrightarrow CH_3(CH_2)_3CH = CH_2 + CO + 2H_2$$

However, von Braun[3] obtained a hexene by gently heating *n*-hexyl trimethyl ammonium hydroxide, which showed a boiling point of 62–63° and which he regarded as the true α-hexene, although he was unable to prove the constitution of it, owing to the small quantity obtained, 1.5 g. Since the method of preparation employed by us readily yielded the pure α-hexene, free from isomers, we were able to prove its constitution. Its physical properties are as follows:

B. p. 756 mm. 60.5–61.5°; $n_D^{20°}$, 1.3821; $d_{20}^{20°}$, 0.6830.

The following method of preparation indicates the procedure followed with but little variation in the preparation of the α-olefins: Normal propyl bromide, 85 g., was added to 18 g. magnesium turnings in 500 cc. of ether. After the magnesium compound had formed the reaction mixture was chilled and 68 g. allyl bromide in 60 cc. ether was gradually added during a period of 24 hours. The ether solution was poured from the residue of magnesium bromide to avoid any possibility of isomerization by warming with the magnesium salt, and most of the ether distilled. Ether was completely removed from the remainder by washing out several times with large volumes of water, and the hydrocarbon distilled. Only 3 cc. were obtained boiling below 60.5°. The yield was 34 g.; b. p., 60.5–61.5°.

The constitution of the hydrocarbon was shown by a method which has not been employed heretofore, so far as we know, in determining constitution.[4] The modification of the older methods which we have employed consists in the addition of hypochlorous acid to form the chloro-

[1] *Chem. Zentr.*, 79, II, 1854 (1908).

[2] *Ibid.*, 1911, II, 1017.

[3] *Ann.*, 382, 22 (1911).

[4] Oxidation of the olefin by chromic acid can not be employed in this case owing to the fact that rearrangement of the α-olefin to the β-isomer has been observed with iso-α-pentene.

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hydrine (both the α-chloro, β-oxy- and the α-oxy-β-chloro derivatives are probably formed) and the conversion of the chlorohydrine into the glycol by warming in a dilute aqueous solution of sodium bicarbonate. The yield of glycol is much superior to that obtained by the old permanganate oxidation method.[1] The chlorohydrines are readily made by shaking the hydrocarbon with an aqueous solution of hypochlorous acid made by adding boric acid to a cold solution of bleaching powder.

Alpha hexene, 52 g., was slowly added to 100 cc. 85% sulfuric acid at 15° during a period of 20 minutes. The hydrocarbon dissolved completely to a clear, viscous, amber-colored solution. The solution was poured into 4 volumes of water and cracked ice. With this amount of water the large supernatant layer consisted of hexyl sulfuric acid and free alcohol. On adding about 6 volumes of cold water to this supernatant layer, the hexyl sulfuric acid passed into solution and the free hexyl alcohol layer separated. This alcohol or "acid oil" layer was washed thoroughly with water. The aqueous solution was extracted with ether to remove all dissolved free hexyl alcohol, obtaining a total of 28.0 g. oil, having $d_{20°}^{20°}$, 0.823. The alcohol distilled principally at 134–138° and acetylated readily in acetic anhydride to the secondary hexyl acetate boiling point, 154–158°.

The aqueous solutions containing the hexyl sulfuric acid (as such it proved to be) were combined and treated with an excess of barium carbonate, filtered with suction, and the aqueous solutions gently evaporated during about 48 hours at 35–40°. The dry crystalline barium salt weighed 44 g. It is very soluble in water, the concentrated aqueous solutions having a marked syrupy consistency.

Calc. for $(C_6H_{13}OSO_3)_2Ba$: Ba, 27.40. Found: 27.23.

Iso-α-heptene, $\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CHCH_2CH_2CH = CH_2$. — This hydrocarbon, which is new, was made by acting upon magnesium isobutyl bromide with allyl bromide in the manner already described for α olefins. This heptene boils at 85–86° and has $d_{15°}^{15°}$, 0.7160. By treating 15 g. of the hydrocarbon with 25 g. of 85% sulfuric acid, we obtained 7.3 g. polymers, $d_{15°}^{15°}$, 0.7933, which proved to consist mostly of the dipolymer, as indicated by the boiling point 220–224°, at which temperature about 5 g. of the oil distilled.

γ-Heptene.—This hydrocarbon was made by starting with the *symmetrical* alcohol dipropyl carbinol, converting this into the iodide and removing hydriodic acid by caustic alkali in the usual manner.[2] It will be

[1] A separate paper on this method is in preparation.

[2] Splitting off water from this alcohol by refluxing and distillation with iodine is too slow in this case to be of practical value. 90 g. of the alcohol and 0.3 g. iodine gave only 0.5 g. water in 5 hours at 145°.

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seen that owing to the symmetry of this compound, simple removal of hydriodic acid and barring molecular rearrangement, only the olefin γ-heptene should result. After purification, the boiling point was found to be 93–95° (previously noted 95.5°) and $d_{20°}^{20°}$, 0.7020.

A quantity of the heptene, 68 g., was slowly added during 30 minutes to 200 g. of 85% sulfuric acid, the reaction mixture being kept chilled to 15°. The oil dissolved completely. The clear, viscous amber-colored solution was added to 4 volumes of ice and water and the supernatant layer of free alcohol and heptyl sulfuric acid and water weighed 188 g.; calculated for the monoheptyl ester, 136 g. On diluting this sulfuric ester layer with 6 volumes of ice water there was obtained, after the usual washing with water and extracting the aqueous acid solutions, 42.0 g. alcohol which, on distillation under 26 mm. pressure, boiled mostly at 75–77°. The alcohol acetylates quantitatively with acetic anhydride. The water-soluble barium salt, isolated as described above, weighed 81.0 g.

Calc. for $(C_7H_{15}OSO_3)_2Ba$: Ba, 26.0. Found: 26.29.

It is worthy of note that with both α-hexene and γ-heptene no polymers were formed.

γ-Ethyl-β-pentene, $\begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}\!\!>\!C = CH - CH_3$.—This hydrocarbon, boiling point 97–98°, was made by the dehydration of triethyl carbinol,[1] and, owing to the symmetry of this alcohol, the derived olefin is exceptionally pure. This heptene was treated at 0° with sulfuric acid, sp. gr. 1.84. The behavior of this olefin is markedly different from the duodecene described below and it is noteworthy that the 2 hydrocarbons possess similar constitutions. To 102 g. of the hydrocarbon 120 g. of the acid were slowly added with vigorous mechanical agitation. After standing about half an hour, 21 g. of clear supernatant oil were removed and treated again with an equal volume of sulfuric acid, sp. gr. 1.84. After treatment, the residual oil was removed, washed and distilled, obtaining:

Fraction.	B. p.	Volume, cc.	Sp. gr.
I	to 210°	3	....
II	210–220°	7.5	0.793 dipolymer
III	220–250°	4.0	....
Residue	....	1.5	....

The viscous amber-colored sulfuric acid solution was run into cracked ice and 82 g. of crude alcohol, sp. gr. 0.820, were obtained. On washing with dilute alkali, 7 g. were removed (see below). The crude alcohol thus obtained was light yellow in color and smelled strongly like the original tertiary alcohol. Distillation gave the following:

[1] Saytzen, *J. prakt. Chem.*, [2] **57**, 38 (1898).

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Fraction.	B. p.	Wt. g.	Sp. gr.
I	90–115°	20.5	0.773
II	115–130°	26.3	0.786
III	130–150°	9.6	0.789
IV	150–190°	1.7	...
V	190–220°	6.9	0.862
Residue	....	9.5	0.896

By redistilling 3 times, the alcohol Fractions II and III were almost completely decomposed, with splitting off of water to the unsaturated hydrocarbon. Of the 2 alcohols whose formation is possible, $(C_2H_5)_2C\begin{matrix}OH\\CH_2CH_3\end{matrix}$ and $(C_2H_5)_2CHCHOH.CH_3$, the former only is known, and the instability of the alcohol formed in this case indicates that it is the tertiary one. That this tertiary alcohol should be formed in this case in conc. sulfuric acid is noteworthy as indicating that tertiary alcohols are formed rather than secondary. In the same way the α-olefins form secondary not primary alcohols.

It was assumed that the aqueous acid solution contained heptyl sulfuric ester. Accordingly, it was further diluted to 0.5 liter and thoroughly extracted with ether until all odor of the camphor-like tertiary alcohol was removed. Half of the solution was distilled with steam and 3.0 g. of oil obtained, having the characteristic odor of the tertiary alcohol. The other half of the solution was further diluted and the barium salt made in the usual manner, obtaining, by very gentle evaporation of the filtered aqueous solution at about 50°, 6.5 g. of the salt. Analysis showed:

Calc. for $(C_7H_{15}OSO_3)_2Ba$: Ba, 26.0. Found: 27.6.

The somewhat high per cent. of barium found is undoubtedly due to slight decomposition of the salt.

Tetramethyl Ethylene, $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C = C<\!\!\begin{matrix}CH_3\\CH_3\end{matrix}$.—This hexene was made by decomposition, with removal of water, of dimethyl isopropyl carbinol by means of acetic anhydride. Three fractional distillations of the resulting hydrocarbon gave a very pure product boiling at 73–74° $d_{20°}^{20°}$, 0.7075.

A quantity of the olefin, 46.5 g., was slowly added to 150 g. of 85% sulfuric acid at 0° during one hour's time. Solution is markedly more rapid and energetic than in the case of α-hexene. The crystals of monohydrated sulfuric acid gradually disappeared and the hydrocarbon dissolved completely. On standing for one hour, the temperature rising to 15°, a colorless oil layer weighing 37.6 g., $d_{20°}^{20°}$, 0.7750, separated. Fractional distillation of this oil showed its principal constituent to be the dipolymer,

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Fractions.	Weights.
to 175°	4.0 g.
175–180°	18.5 sp. gr. = 0.762
180–200°	5.0
200–220°	4.5
Residue	4.5

On diluting the acid layer with water and cracked ice only 1.6 g. of alcohol were obtained (including that recovered by ether extraction) which possessed the strong camphor-like odor of the original carbinol. The soluble barium salts, recovered in the usual way, weighed 20.2 g. (accounting for about 7.1 g. of the original olefin). This salt proved to be noticeably more unstable than the salts derived from secondary alcohols, as from α-hexene, γ-heptene and the like. It decomposed slowly on standing at room temperature and analysis showed a percentage of barium somewhat higher than required by the theory, a result readily explained by the instability of the salt.

Calc. for $Ba(OSO_3C_6H_{13})_2$: Ba, 27.4. Found: 28.6.

Sulfuric Acid, 100% H_2SO_4, on Hexenes.—The hexenes employed in this experiment were not pure and were prepared from a monochlorohexane fraction derived from a petroleum hexane fraction. The crude hexenes boiled at 58–70° and had a specific gravity of 0.700. To 200 g. of the acid 70 g. of the hexene were slowly added at —10°. A total of 62 g. was recovered as polymers and these distilled over a wide range up to 250° under 20 mm. pressure. Polymerization evidently proceeds much farther with acid of this concentration, the last fraction being a heavy viscous oil, sp. gr. 0.901. We were surprised that the amount of water-soluble alkyl sulfuric acid was so low, only 3.2 g. of soluble barium salt being obtained. Considerable oxidation was noted, even at this low temperature, as indicated by the evolution of sulfur dioxide and the formation of 12% of tarry matter not distilling up to 250° at 20 mm. pressure.

The absence of alcohols in the products of this experiment is significant, as discussed in the first part of this paper. A small amount of "acid oil" which separated on diluting the acid with cracked ice was examined for alcohols by acetylating gently. One gram of the oil so treated required 39 mg. caustic potash and 1 g. hexyl acetate requires 389 mg. potash. Heating the acid oil liberated sulfur dioxide at the rate of 0.029 g. sulfur dioxide per gram oil, thus partly accounting for the small saponification value of the acetylated sample.

A more conclusive result regarding the non-formation of alcohols when water-free acids are employed was obtained by the use of benzene sulfonic acid, thus avoiding the oxidation and energetic polymerization of the pure anhydrous sulfuric acid.

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Benzenesulfonic Acid and γ-Heptene.—In view of the formation of dialkyl esters of sulfuric acid by the action of sulfuric acid on an excess of the olefins, it seemed to us quite probable that benzenesulfonic acid would behave in a similar way. To 25 g. of γ-heptene, prepared as described above, an excess of pure crystalline benzenesulfonic acid was added at room temperature. Solution with evolution of heat took place and after standing about 2 hours, the excess of the sulfonic acid was removed from the resulting heavy oil by washing with water and dil. sodium bicarbonate solution. The resulting ester, $d_{20°}^{20°}$, 0.979, could not be distilled at 20 mm. without decomposition, sulfur dioxide being evolved. Saponification of 1.922 g. required 393 mg. caustic potash, or 204.5 mg. per gram; the benzenesulfonic ester requires theoretically 254 mg. The crude ester evidently contained a little unchanged heptene, but the strong odor of the secondary heptyl alcohol, very noticeable even when small traces are present, was totally absent. Saponification of the ester with aqueous caustic soda readily yields heptyl alcohol, b. p. 134–136° and probably contains both dipropylcarbinol and ethylbutylcarbinol.

α-Octene.—Heptylaldehyde, purified from commercial oenanthol, was condensed with bromoaceticester and zinc to the β-oxypelargonic acid ethylester in dry benzol according to Wallach's modification of the Reformatsky reaction. The oxy-ester was saponified by sodium methylate in 20 volumes of methyl alcohol. The oxy-acid was made by Wagner[1] in another way, and the product described by him as melting at 48–51° probably was impure, since the oxy-acid obtained by us, recrystallized from ether-ligroin, melted sharply at 58.5°. The yields were poor. From 228 g. of heptylaldehyde we obtained 114 g. of the oxy-acid. This was heated with acetic anhydride, as recommended by Wallach, giving 82 g. of the unsaturated acid. We find that this α-octene α-carbonic acid is relatively stable. It was described by Fittig[2] simply as an oil. We find that it distills with very little decomposition at 220–223°.

To 52 cc. of the octene, b. p. 122–124°, sp. gr. 0.7240, was added 50 cc. of 85% sulfuric acid, H_2SO_4, maintaining the mixture at 20°. Very little discoloration and very little heating effect were noted. The oil layer, 38 cc., very faintly yellow, after washing until neutral, had the specific gravity 0.854. On attempting to distil this oil, it quickly blackened and gave off sulfur dioxide, suddenly and with such violence that the whole mass frothed over into the receiver. This was carefully redistilled, obtaining 32 cc., b. p. 122–124°. We hope to repeat this experiment and determine the per cent. of the sulfur dioxide, in view of these unexpected results.

The acid layer yielded only 2.5 cc. of oil, having the odor of secondary

[1] *Ber.*, **27**, 2436 (1894).

[2] *Ann.*, **227**, 80 (1885).

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octyl alcohol. This was dried and treated with phenylisocyanate, the phenylurethane, recrystallized from methyl alcohol, melting at 238°.

With 96% sulfuric acid, a greater percentage of polymers was formed, and, as in the other cases studied, largely the dipolymer. From 30 cc. of the octene, 24 cc. "insoluble" oil were recovered, which on distillation gave:

		Boiling point.	Per cent.
I.	Unchanged hydrocarbon	120–125°	16
II.	Intermediate fraction	125–195°	9
III.	Crude dipolymer	195–230°	32
IV.	Higher polymers	above 230°	42

Although the boiling point of the α-octene, made as indicated above by heating α-octene-α-carbonic acid, agrees with the boiling point of α-octene described in the literature, we are inclined to believe that this so-called α-octene may be the β-olefin, since, as already pointed out, heat causes the olefins to rearrange. The method of preparation for this octene described in the literature, namely, decomposition of secondary octyl iodide, also indicates that the known hydrocarbon of this boiling point may be the β-compound.

α-Isooctene.—This hydrocarbon, which is new, was made with a very satisfactory yield by the condensation of magnesium isoamyl bromide and allyl bromide in the manner discussed above. Its physical properties are as follows:

B. p., 111–112°; $d_{4°}^{20°}$, 0.7125; $n_D^{20°}$, 1.3986

Sixty grams of the hydrocarbon were slowly treated with 225 g. of 85% sulfuric acid at 15°. The clear yellow acid layer was poured into cracked ice, thus separating 9.0 g. of the secondary alcohol, β-oxy-ζ-methyl heptane. Owing to the small quantity of this alcohol available, the constitution tentatively ascribed to it was not verified. It acetylates readily in acetic anhydride, yielding an acetate having a pleasant fruity odor, boiling at 190–193°.

The oil layer separated from the acid weighed 48 g.; sp. gr., 0.800. The oil, light yellow in color, was distilled at 16 mm., giving 8.1% unchanged octene, 53.3% dipolymer $C_{16}H_{32}$; sp. gr. 0.798, and b. p. 112–114° at 16 mm. The impure higher polymers, 28.6%, had a specific gravity of 0.804. The dipolymer showed a bromine absorption, in acetic acid solution, of 74; calculated for one double bond in $C_{16}H_{32}$ = 71. Only 1.5 g. soluble barium octyl sulfate were recovered from the acid solutions.

The relatively large amount of polymers and small amount of alcohol and octyl sulfuric esters, as compared with the behavior of α-hexene, is worthy of note.

β-Methyl-β-undecene, $C_{12}H_{24}$, $C_8H_{17}CH = C\begin{matrix}CH_3\\CH_3\end{matrix}$. — Methylnonyl

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ketone was isolated from oil of rue by means of the sodium bisulfite compound.[1] By acting upon the ketone with magnesium methyl iodide, the tertiary alcohol was obtained and on distilling this alcohol with a trace of iodine, a nearly theoretical yield of the unsaturated hydrocarbon was obtained. Since this hydrocarbon is new, we give its constants as follows:

B. p. at 752 mm., 210–211.5°. $D_{4°}^{20°}$, 0.7590; $n_D^{20°}$, 1.4270 MR; calc. for $C_{12}H_{24}$: 56.93. Found: 56.51. Bromine number, calc. for $C_{12}H_{24}$: 95.0. Found: 95.0.

That the constitution of the hydrocarbon is in fact that noted above was shown by oxidizing with chromic acid solution in the usual manner, distilling with steam and proving the presence of acetone in the distillate by the iodoform reaction and the formation of dibenzylidene acetone; m. p., 111°.

A quantity of the hydrocarbon weighing 79 g. (104 cc.) was treated slowly with 130 g. of 85% sulfuric acid at 20°. A viscous, light yellow emulsion was obtained which, however, quickly separated on standing a few minutes. The mixture was vigorously shaken for 20 minutes, but after standing 10 minutes longer there occurred a complete separation into a clear straw-colored acid layer and a *water-white, viscous* oil layer, the latter measuring 95 cc. After washing with water and dil. alkali and drying, this "insoluble oil" weighed 75.5 g.; sp. gr., 0.799. The increase in specific gravity is quite marked. The oil was then heated to 200° to decompose any sulfuric acid esters present, but only 0.028 g. sulfur dioxide was obtained and the oil was only very slightly discolored. It was then distilled under 28 mm. pressure and the following fractions were obtained:

Fraction.	Volume, cc.	Temperature.	$n_D^{20°}$.	Sp. gr.
I	19	105–110°	1.4270	0.7590
II	7	110–230°	..	..
III	62	230–234°	1.4510	0.814
IV	4	234–242°	..	..
Residue	2	....	..	..

These results were quite surprising in showing that the original hydrocarbon had been converted into the *dipolymer* and practically no higher polymers had been formed. The polymerized oil, even before distillation, was water-white in color and, moreover, this effect had been produced accompanied by a loss to the sulfuric acid of but 4.4% by weight. These results were so entirely at variance with the generally accepted notions of the behavior of petroleum olefins to sulfuric acid that the experiment was repeated, employing sulfuric acid of 96% concentration. In the above experiment, the loss to the acid was so small that it was not at-

[1] Previous workers have stated that this ketone reacts only very slowly and with difficulty with sodium bisulfite solution. We find that if the bisulfite solution contains 20 to 30% of ethyl alcohol, the reaction can be completed in a few minutes.

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tempted to isolate the acid oil, in fact only a few drops of oily substance, having an odor suggestive of the higher alcohols, were obtained on diluting the acid layer with water.

The dipolymer $C_{24}H_{48}$ is also an unsaturated hydrocarbon as was indicated by its behavior toward cold alcoholic potassium permanganate and toward a solution of bromine in acetic acid. Titration of 3 cc. of the dipolymer in acetic acid, with a solution of bromine in acetic acid, gave a bromine number of 43; calc. for $C_{24}H_{48}$: 47.5.

Concentrated sulfuric acid, sp. gr. 1.84, gives practically the same results as the 85% acid. Owing to the fact that only a small quantity of the original hydrocarbon was available, the experiment could not be made as complete as the one above. However, on treating 15 cc. of the oil at 20°, the loss, after agitating thoroughly for 20 minutes, was 1.5 cc., or about 10% by volume. The supernatant oil was very faintly yellow, and on distillation proved to consist of the dipolymer to the extent of about 85%.

Hexadecene from Spermaceti.—A hexadecene was made from purified spermaceti, essentially cetyl palmitate, by making use of the well-known method of destructive distillation of palmitic acid esters. The crude product of the destructive distillation was chilled to remove most of the free palmitic acid, washed thoroughly with hot dil. caustic soda and distilled *in vacuo*. The crude hexadecene had the following properties:

B. p. 130–150° at 18 mm.; $d_{20°}^{20°}$, 0.8850; bromine number (in acetic acid solution), 68.1.

In view of the method of preparation of this hydrocarbon it probably contains little or none of the α-hexadecane which would normally be first formed, but one or more isomers of the α-olefin.

With 85% sulfuric acid this mixture of unsaturated hydrocarbons remains practically unchanged after thorough agitation at ordinary temperatures. From 160 g. of the oil we recovered 148 g. unchanged oil distilling within the original range above noted, 10 g. higher boiling residue which naturally consisted partly of unchanged material, and 2 g. loss. This loss occurred largely in handling. On diluting the acid solution only a slight turbidity was noted and no separation of acid oil or tar.

With more concentrated sulfuric acid, sp. gr. 1.84, considerable polymerization occurred. On agitating the oil and acid at room temperature, about 22°, the mixture warmed slightly, but no tar formation, charring or blackening was observed. The acid layer which separated on standing gave no acid oil on diluting with ice water. From 86 g. of the crude hexadecene we obtained 84 g. of a very viscous oil which, on fractionating at 18 mm., yielded the following: 130–155°, 25.0%, considered as unchanged oil; 155–320°, 52.4% mostly dipolymer $C_{32}H_{64}$; residue above 320°, 19 g. or 22.6%. This residue was particularly interesting from the

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petroleum technologists' point of view, as it had a viscosity equal to very heavy cylinder oil of about 16 to 18 degrees Engler. It seems certain, therefore, from the results found, particularly in this case and with the duodecene described above, that so far as the action of sulfuric acid on olefins is concerned, the refined oils should show greater viscosities than the original distillates, but this difference is usually more than counterbalanced by removal of other substances, in some cases asphaltic material. That refining of crude kerosenes increases their flash points, is well known and the theory which had already been advanced to explain the change, is supported by the results we find.

The marked differences in their behavior to sulfuric acid, between the hydrocarbons of 12 to 16 carbon atoms and the unsaturated fatty acids, such as oleic acid, is difficult to account for.[1]

Menthene.—By slowly distilling menthol with 1% of iodine, a molecule of water is readily removed from the menthol, forming a menthene, b. p. 169–170°, $d_4^{20°}$ 0.811, and probably identical with the menthene of this boiling point studied by Wallach.[2] A quantity, measuring 119 cc. of the hydrocarbon was treated with 100 cc. of 85% sulfuric acid, and thoroughly shaken for 20 minutes. After standing until the 2 layers had become clear, the supernatant oil measured 101 cc. and after washing and drying had a specific gravity of 0.867 at 20°/4°. This oil was fractionated, obtaining 35% unchanged menthene and 55% dimenthene $C_{20}H_{36}$, b. p. 310–315°, sp. gr. 0.899, $n_D^{20°}$ 1.4795. Like the other dipolymers previously obtained, the dimenthene was unsaturated but the bromine or iodine absorption numbers could not be obtained, owing to decomposition of the halogen derivatives and discoloration of the acetic acid solution.

On adding the sulfuric acid solution to cold water, 12.5 g. of oil separated, smelling strongly of *menthol*. Distillation of this oil gave a small fraction, 2.0 g., b. p. 165–180°; about 1.0 g. from 180–200°; 3.0 g. from 200–215°; and 5 g. residue. The fraction 200–215° had a strong odor of menthol, but no crystals separated from it on cooling at —15°.

Effect of Time on Yield of Polymers.—The yield of alcohol and polymers obtained in Expts. 2 and 4, Table IV, indicates that on standing, the yield of polymers increases at the expense of alcohol. This is well shown by the behavior of secondary octyl alcohol, β-oxy-*n*-octane. To 50 g. of the alcohol, 100 g. conc. sulfuric acid, sp. gr. 1.84, were gradually

[1] According to unpublished results of this laboratory, the unsaturated fatty acids are much easier hydrogenated than are the unsaturated hydrocarbons. Our first surmise was that the petroleum olefins contained traces of sulfur compounds, which poisoned the catalyst, but a mixture of cottonseed oil and highly unsaturated kerosene, iodine number 55.2, purified by distillation over fine copper oxide yielded a semi-solid mixture of solid hydrogenated cottonseed oil and the kerosene practically unchanged.

[2] *Ann.*, 300, 282 (1898).

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added during 10 minutes, keeping the mixture cooled to 20°. The solution, which was originally clear, but dark brown in color, became turbid, and oil separated, the volume of which was read at frequent intervals. The solution became quite dark in color but no tarry matter was formed. The supernatant layer of oil was light amber in color.

FORMATION OF POLYMERS FROM SECONDARY OCTYL ALCOHOL.

Time, minutes.	% by volume.
15	8.0
30	17.0
45	40.0
60	50.0
85	52.0
105	56.0
135	62.0

On distillation the oil gave about 40% of the dipolymer $C_{16}H_{32}$, distilling at 275–285°, the remainder consisting of slightly viscous higher polymers, probably the tripolymer $C_{24}H_{48}$.

1. **Methyl-Δ_1-cyclohexene.**—Only a small quantity of this hydrocarbon was available. The oil, 15.6 g., having the b. p. 105–106° and $d^{20°}_{20°}$, 0.820, was treated with 35 g. of 85% sulfuric acid at 0°. The insoluble polymers weighed 11.5 g. and on redistillation 80% of this oil boiled at 255–260°, $d^{20°}_{40°}$ 0.906, evidently consisting of the dipolymer $C_{14}H_{28}$. The acid layer on diluting with ice water yielded 4.0 g. crude alcohol, having the mint-like odor of the tertiary alcohol methyl (1) cyclohexanol (1).

Cinnamic Acid.—We have found no reference to the addition of water to cinnamic acid by means of dil. sulfuric acid. We find that 85% and 96% sulfuric acid neither polymerizes or hydrates the substance. After thoroughly agitating the mixture and allowing to stand at 25° for 24 hours, the solid material was filtered with suction, the acid filtrate diluted with water and extracted with ether. From 100 g. of cinnamic acid there was obtained in this way about 2.0 g. of substance which proved to be unchanged cinnamic acid. Also, fractional crystallization of the solid material gave no evidence of the presence of the lower melting hydroxy acids.

Dichloroethylene.—This substance reacts slowly at 20° with 85% and with 96% sulfuric acid. On agitating equal volumes, 150 cc. of the substance and the acid, the acid layer becomes discolored and hydrogen chloride is evolved. After agitating the mixture half an hour, separating and washing as usual, the loss in volume of the dichloroethylene was 6%. Distillation showed that no polymerization whatever had occurred.

The sulfuric acid solution was run into 10 volumes of cold water. A strong aldehyde odor was noticed. The aqueous solution was distilled with steam and the first 25 cc. of distillate examined. It smelled strongly of chloroacetaldehyde, reduced ammoniacal silver solution giving a mirror,

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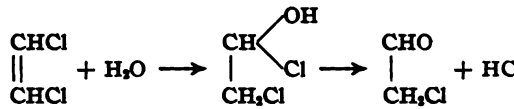
and an oily precipitate with phenylhydrazine solution. The reaction is evidently as follows:



The Terpenes, α- and β-Pinene, Limonene and Myrcene.—A quantity of ordinary turpentine was distilled, collecting the fraction 155–159°. This was assumed to be largely ordinary or α-pinene. As usually carried out, the reaction of conc. sulfuric acid and turpentine is so energetic that the temperature rapidly rises and oxidation with the separation of carbon, tar, sulfur dioxide, etc., occurs. However, at 0° with 85% sulfuric acid, the reaction can be readily controlled and the reaction mixture maintained at this temperature. Under these conditions the principal reaction products are the dipolymer $C_{20}H_{32}$, distilling at 170–175° under 15 mm. pressure and the very viscous tripolymer. On distilling the forerunnings, a marked odor of borneol was noticed, but no crystals could be isolated. To 79 g. of the pinene, b. p. 155–159°, $d_4^{20°}$ 0.8630, there was slowly added, at 0° with vigorous stirring, 150 g. acid. The reaction mixture was so viscous that it was allowed to stand several hours at about 5° in order to separate the two liquids. In all 72 g. oil were recovered, which on distillation at 15 mm., resolved itself chiefly into the two fractions

170–175°	32 g.	Sp. gr. 0.938, dipolymer, $C_{20}H_{32}$
175–245°	7 g.	Intermediate
245–260°	18 g.	Probably tripolymer, $C_{30}H_{48}$, very viscous

In another experiment in which 72% sulfuric acid was employed at 25°, a yield of 62% of the dipolymer, b. p. 170–175° at 15 mm., was obtained.

A quantity of β-pinene[1] behaved in an entirely similar manner. In these experiments we were unable to note any difference in the behavior of the two isomers, in other words, as between the Δ_6 and $\Delta_{1(7)}$ structures.

From 250 g. β-pinene we obtained 239 g. liquid, sp. gr. 0.940, by treating as above with 85% acid, which on distilling at 12 mm. gave:

B. p.	Wt.	Sp. gr.	n_D^{20}.	Product.
55– 70°	21.5	0.851	1.4670	$C_{10}H_{16}$
70–165°	14.8	0.872	1.4725	Intermediate
165–171°	113.2	0.935	1.4838	$C_{20}H_{32}$
171–285°	62.0	0.951	..	Very viscous

The further study of these dipolymers was not undertaken.

Limonene, isolated from sweet orange peel oil, behaved in a very similar manner to the pinenes. From 185 g. we obtained 174.5 g. of the mixture of polymers, sp. gr. 0.934, which on distilling at 12 mm. gave:

[1] Furnished to us through the kindness of Dr. A. W. Schorger of the Forest Products Laboratory.

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B. p.	Wt.	Sp. gr.	n_D^{20}.	
60–167°	20.5	0.821	1.4718	Viscous, $C_{20}H_{32}$
167–172°	74.2	0.939	1.4828	
172–245°	26.0	0.945	..	
245–260°	29.0	0.954	..	Very viscous, dries to touch by air oxidation

Myrcene was prepared by the decomposition of linalool with removal of water by distilling with a very small quantity of iodine. From 270 g. linalool there were obtained nearly the theoretical quantity of water by slowly distilling with 3 g. iodine during 2 hours. Fractional distillation gave 103 g. myrcene, b. p. 165–167°; a small fraction, 24 g., b. p. 167–177°, consisting apparently of a mixture of myrcene and limonene; and about 143 g. unchanged linalool and polymers. The reaction of myrcene with 85% sulfuric acid was so energetic at 0° that we were unable to prevent tar formation, oxidation, carbonization, etc. In this respect its behavior is like the known behavior of cyclopentadiene and cyclohexadiene.

Freezing-point curves, camphene and trichloroacetic acid.

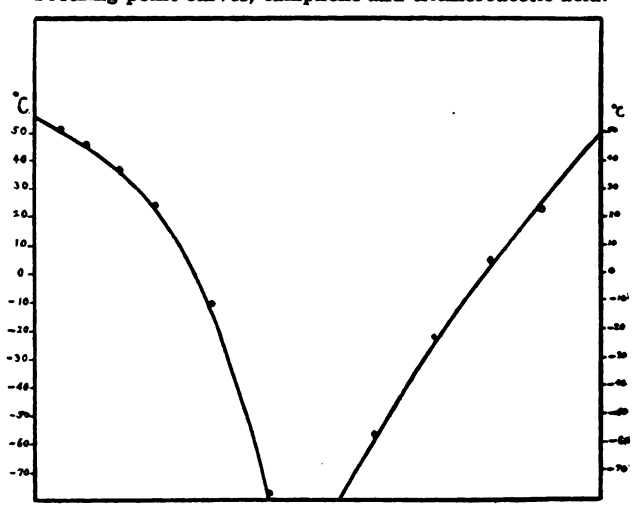

Fig. 1.

The freezing-point curves for camphene and trichloroacetic acid are given in the accompanying figure. Trichloroacetic acid is known to be somewhat reactive toward olefins, but no attempt is made here to review this behavior.[1]

The action of 85% sulfuric acid on styrene results only in the resinous polymer. No trace of either primary or secondary phenylethyl alcohol is formed, as the fragrant odor of both these alcohols is readily observed when present only in traces. From 23 g. pure styrene with 25 g. of the acid at 5° we obtained only the polymer. No sulfuric esters were formed.

Both 96% and 85% conc. sulfuric acid are without action on fumaric acid. Ten grams fumaric acid were vigorously shaken with 25 g. of 96% sulfuric acid at room temperature, the mixture poured into ice water and 9.8 g.

[1] Timofeev and Kravtzov, *Chem. Abs.*, 9, 2896 (1915); 11, 788 (1917).

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unchanged fumaric acid recovered. The filtrate was carefully examined for coumalic acid, but without result.

A New Decene, $(CH_3)_2CH.(CH_2)_4.CH(CH_3)_2$.—In the preparation of iso-α-octene, described above, there were obtained 17 g. of decene in a preparation in which 250 g. isoamyl bromide were converted into the Grignard magnesium compound. Its formation is due to the decomposition of the isoamyl magnesium bromide after the manner common to the higher alkyl halides.

$$(CH_3)_2CHCH_2CH_2MgBr + (CH_3)_2CHCH_2CH_2Br \longrightarrow MgBr_2 + (CH_3)_2CH.(CH_2)_4.CH(CH_3)_2.$$

Its constitution was not proven, but inferred from the manner of its formation. Its constants are as follows:

B. p., 156.5–157.5°; $n_D^{20°}$, 1.4006; $d_{20°}^{20°}$, 0.7270.

Part II. The Action of Sulfuric Acid on Petroleum Distillates.

General Discussion of the Refining Problem.—When petroleum oils are agitated with conc. sulfuric acid, a rise in temperature is commonly observed. In the case of low boiling, highly unsaturated oils, such as oil gas "drips" and many light oils rich in benzene, this may be sufficient to cause boiling, and in this case is invariably accompanied by the evolution of sulfur dioxide. With lubricating oils and with less highly cracked light oils, this rise in temperature is not so marked. After agitation, the emulsion is allowed to stand and a heavy viscous layer containing most of the sulfuric acid separates. When this heavy layer is run into water, an oil mixture is precipitated, which, in the case of the lower boiling petroleum distillates, is a yellow fluid oil having a very characteristic, sweetish odor, and which darkens rapidly on exposure to air. The more viscous distillates yield in this way a tarry "acid sludge." The customary refinery practice is to burn these acid oils and tars under the stills. The diluted acid is evaporated and concentrated for reuse, but organic matter continues to separate during the concentration and causes considerable loss of acid by reduction, accompanied by charring, and is a great source of trouble to the refiner.

Our investigation of mono-olefins as high as $C_{24}H_{48}$ in complexity, and including representatives of the 5 possible types, shows that tars are *not* formed by the action of ordinary conc. sulfuric acid on them at ordinary temperatures. On the other hand, tars *are* formed from highly unsaturated distillates, even the low boiling ones, which have been made by

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heating oils to very high temperatures, 600° to 800°, as in the manufacture of oil gas. Such light oils are rich in benzene and its homologs. *The tars formed* on treating such oils are apparently due to the presence of diolefins. Acetylene homologs are not usually present. The unsaturated oils up to and including kerosene distillates made by cracking at lower temperatures, 400° to 420°, as in pressure distillation of heavy oils, give fluid "acid oils" when treated with sulfuric acid.

It is a fact known to most refiners that on refining gasoline and kerosene, particularly the products made by cracking, the resulting refined products have higher specific gravities than the original oils, although if the refining operation consisted essentially of the removal of olefins, the refined product should be lighter than the original, as is, in fact, the case when the liquid sulfur dioxide method is employed.[1] We have shown that when the refining is done in closed vessels, so as to preclude loss of the more volatile constituents by evaporation, the same change is noted and this is due primarily to the first of the following causes: The presence in the refined product of heavier polymers of the unsaturated hydrocarbons, originally present, as the conversion of duodecene $C_{12}H_{24}$, sp. gr. 0.759, to the dipolymer $C_{24}H_{48}$, sp. gr. 0.814, and also to the presence in the refined product of dialkyl esters of sulfuric acid. These esters, $\begin{matrix} RO \\ RO \end{matrix}\!\!>\!SO_2$, are, of course, neutral and are not removed by washing with aqueous alkalies. We have also shown that the proportion of these sulfuric esters in the refined products is roughly *inversely* proportional to the relative amount of sulfuric acid employed, as is readily apparent on considering the two equations

$$\begin{matrix} RCH \\ \| \\ R_1CH \end{matrix} + H_2SO_4 \longrightarrow \begin{matrix} RCH_2 \\ | \\ R_1CHOSO_3H \end{matrix} \qquad (1)$$

$$\begin{matrix} RCH \\ \| \\ R_1CH \end{matrix} + \begin{matrix} RCH_2 \\ | \\ R_1CHOSO_3H \end{matrix} \longrightarrow \begin{matrix} RCH_2 \\ | \\ R_1CH - O.SO_2.OHC - R_1 \end{matrix} \begin{matrix} H_2C - R \\ | \\ \\ \end{matrix} \qquad (2)$$

That saturated hydrocarbons are sulfonated by fuming sulfuric acid is well known from the work of Worstall, Markownikoff, and others. This question, however, is not part of the present problem. It has been claimed by McKee[2] that saturated hydrocarbons may be sulfonated and that, for example, kerosene may be sulfonated by ordinary conc. sulfuric acid by vigorous shaking. We have never had in our possession any saturated hydrocarbons which would exhibit such behavior to ordinary sulfuric acid. Pure normal heptane, isolated from *Pinus*

[1] Schultz, *Petroleum*, 5, 205, 446 (1909).
[2] *Chem. Ztg.*, 36, 872 (1912).

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sabiniana,[1] was absolutely unaffected by shaking with sulfuric acid, sp. gr. 1.84, at 25° for 48 hours. Also, a sample of di-isopropyl[2] was entirely unaffected when treated in the same manner. With fuming sulfuric acid, 15% SO_3, di-isopropyl lost 32.2% by volume on agitating for 35 minutes at 22°.

The *aromatic hydrocarbons*, which are invariably present in very small proportions, undoubtedly react to a slight extent to form true sulfonic acids, since the higher benzene homologs are very readily sulfonated and one of us has previously shown that the fluorescent substances in petroleum oils are readily sulfonated by ordinary sulfuric acid to give fluorescent, water-soluble sulfonic acids.[3]

It has previously been mentioned by one of us[4] that the objectionable odor of gasoline obtained by pressure distillation is in part due to nitrogen bases. Since the present paper has to do primarily with olefins, we shall merely note here that, on gently heating a quantity of gasoline, made by pressure distillation of heavy Oklahoma fuel oil, with copper oxide, the nitrogen bases present combined with the oxide. The copper oxide compounds yield deep blue aqueous solutions and when the blue solution, or the copper oxide, was treated with alkali, a very strong odor suggestive of pyridine was noticed. Analysis of the copper oxide showed 3.4% nitrogen, or 19.1% calculated as pyridine. Such nitrogen bases naturally pass into the acid "sludge" layer on refining.[5]

In an earlier paper,[6] we noted that gasoline and kerosene which have

[1] Furnished to us through the kindness of Dr. A. W. Schorger of the Forest Products Laboratory.

[2] This hydrocarbon was prepared by the action of anhydrous aluminum chloride on paracymene. It is contained in the fraction boiling at 60–80°. The benzol present may readily be removed by nitrating, and the pure hexane may then be obtained, b. p. 56–58°.

[3] Brooks and Bacon, *J. Ind. Eng. Chem.*, 6, 623 (1914).

[4] Brooks, *J. Frank. Inst.*, 180, 653 (1915).

[5] On heating a mixture of lime and "acid sludge tar" from Oklahoma oil, ammonia was evolved. One kilo of the tar gave 0.51 g. of ammonia, whose identity was confirmed by analysis of the chloroplatinate. It is to be expected that most of the sulfates of ammonia and the simpler bases will remain in solution on diluting with water and would not be found to any great extent in the tars or acid oils. Certain crude petroleums are markedly rich in nitrogen bases. We have noticed that when heavy Mexican oil was subjected to slow cracking distillation, ammonia was evolved toward the end of the process to such extent that it was a great annoyance to persons in the vicinity of the still. Cf. Mabery and Hudson, *Am. Chem. J.*, 25, 253 (1901).

[6] Brooks, *Loc. cit.* Unsaturated or cracked gasolines may be very satisfactorily refined by employing only a relatively small quantity of sulfuric acid followed by redistillation. In other words, it is not necessary entirely to polymerize or remove the olefins present to so improve the crude gasoline in respect to odor and color to be quite equal to good commercial standards. Samples of highly unsaturated and foul-smelling gasolines which we have purified in a manner such as to leave their content of olefins undiminished, as by digestion with fine copper oxide, metallic sodium, etc., have held

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been refined in the usual way and subsequently redistilled, retained its water-white character and agreeable odor much better than such products treated in the same way, but not redistilled, and that this difference is particularly marked in the case of the oils derived by heat cracking processes. We have been able to show the presence in such oils of *neutral esters* of sulfuric acid which are retained by the refined oils, even after washing with alkali until neutral. They are rapidly decomposed at 140°, or higher temperatures, but decomposition also takes place slowly at ordinary temperatures and such oils darken in color on standing and there separates a small proportion of a brown, viscous layer containing a little free acid and considerable resinous matter. When heated, as in distillation, these esters are decomposed with charring and evolution of sulfur dioxide.

The Refining of Cracked Gasolines.—Very early in our work we attempted to refine gasolines made by cracking heavy oils at temperatures

TABLE I.—EFFECT OF REFINING ON THE SPECIFIC GRAVITY OF UNSATURATED GASOLINES.

No.	Specific gravity. Original gasoline.	Specific gravity. After refining and washing.	Loss % by volume.	Remarks.
1.....	0.739	0.743	9.0	From Mexican crude oil by distilling under 150 pounds' pressure
2.....	0.729	0.735	8.2	From Mexican crude oil by distilling under 200 pounds' pressure.
3.....	0.727	0.748	9.8	From heavy Oklahoma fuel oil by distilling under 150 pounds' pressure.
4.....	0.737	0.754	10.1	From heavy Oklahoma fuel oil by distilling under 150 pounds' pressure.
5.....	0.730	0.749	10.6	From heavy Oklahoma fuel oil by distilling under 100 pounds' pressure.
6.....	0.722	0.737	14.0	From heavy Oklahoma fuel oil by distilling under 100 pounds' pressure.
7.....	0.731	0.742	16.2	From heavy Oklahoma fuel oil by distilling under 100 pounds' pressure.
8.....	0.735	0.753	23.0	From heavy Oklahoma fuel oil by distilling under 100 pounds' pressure. Very drastically refined.
9.....	0.737	0.757	28.0	Highly unsaturated gasoline refined with concd. acid and 10% "oleum."

their water-white color and sweet odor for 2 years and are *now better* in both respects than samples of commercial gasoline refined by concd. sulfuric acid and which have stood side by side with the above-mentioned unsaturated gasolines during this same period of time. In the case of oils which do give tars, the use of concd. acid appears to be necessary as the more dilute acid does not hold the tars in solution, as the concentrated acid does. Fair results are obtained by employing other refining agents, such as the anhydrous metallic chlorides (cf. Justice, Eng. patent No. 3572, February 11, 1914). Anhydrous aluminum chloride yields remarkable fine white gasolines and this result is to be attributed also to the ability of this substance to decompose sulfur compounds, organic acids, such as the naphthenic acids, etc.

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up to 550° and under pressures of one to 35 atmospheres, by the usual method of agitating with sulfuric acid, sp. gr. 1.84. The highly unsaturated gasolines were treated successively with 2 to 4 portions of conc. acid, 5% by volume of the gasoline refined. No other constants were obtained on the gasolines noted in the following table, as at the time this work was done no investigation of the refining process was contemplated. We wish to express our indebtedness to Dr. C. W. Clark, who carried out the work noted in Table I.

On redistilling these refined gasolines, abundant evolution of sulfur dioxide was noticed and a large high boiling fraction was obtained. Thus, although the original gasoline had been carefully fractioned and nothing boiling over 150° included, it was noticed that *redistillation after refining yielded 15 to 30% boiling over 150° and the dry point was not reached at 260°.*

Effect of Relative Proportions of Acid and Oil on the Sulfur Content of the Refined Product.—An olefin mixture consisting of hexenes and boiling from 55 to 75° and made from monochlorides boiling from 120 to 140° was used in the following experiments. This hexene fraction had a specific gravity of 0.700 and a bromine absorption number of 182. After thorough agitation with 85% sulfuric acid at 10 to 15°, the supernatant oils were drawn off, washed with alkali and water, and distilled, the sulfur dioxide evolved being neutralized by a standard caustic soda solution in a Peligot tube.

TABLE II.—SULFUR DIOXIDE IN REFINED HEXENE.

Expt.	Vol. oil. Cc.	Vol. H_2SO_4. Cc.	Vol. residual oil.	G. SO_2 on distillation.	% $(RO)_2SO_2$.
1	50	25	32	0.284	4.9
2	50	50	28	0.146	2.9
3	50	100	26	0.094	1.8

That the *concentration* of the acid employed has a marked influence on the amount of sulfur dioxide in the refined and distilled oils has been shown by Hirsch.[1]

A number of samples of cracked gasoline were treated with acid in the usual way to determine approximately the per cent. of the oil polymerized to oils boiling higher than the upper boiling point limit of the original samples, which was 150°.

A series of experiments was carried out to determine the effect of varying concentrations of sulfuric acid on the formation of alcohols, or rather the per cent. of alcohols capable of being isolated from the final reaction products. The olefin employed was a mixture of amylenes and hexenes obtained as a minor product in the conversion of crude monochloropentane into the acetate by heating under pressure with sodium acetate

[1] Cf. Gurwitsch, "Wiss. Grundl. d. Erdölbearbeitung," p. 190.

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TABLE III.—EFFECT OF REFINING CRACKED GASOLINES DISTILLING BELOW 150° ON DISTILLATION-RANGE OF THE REFINED PRODUCT.

No.	Sp. gr. of original gasoline.	Loss to acid; % by volume.	% distillate below 150° in % by vol. of orig. gasol.	% distillate above 150° in % by vol. of orig. gasoline.	Remarks.
1.....	0.728	15.3	52.7	30.0	
2.....	0.737	24.5	55.1	18.4	
3.....	0.735	16.1	62.3	19.6	
4.....	0.738	27.5	33.9	36.6	From kerosene in tubes at 550°.
5.....	0.740	48.0	23.2	27.8	From kerosene over nickel at 550°. 7.8% refined product distilling above 260°.
6.....	0.738	49.0	26.1	24.2	From kerosene over nickel at 550°.

in acetic acid. It contained a small per cent. of saturated hydrocarbons, indicated by the low iodine number 133, but for the purpose of comparing, the so-called hydrating effect of the acid gave sufficiently indicative results. Wischnegradski[1] employed 2 volumes of acid, 50% H_2SO_4, to one of amylene, b. p. 22–45°. We have had little success with acid in concentrations as low as this, in fact we have obtained best results with 85% acid. Also, with respect to temperature, we have found that, in nearly all cases, including pure olefins of the various types up to duodecene, the reaction is very slow below 0°.

TABLE IV.—ADDITION OF WATER TO AMYLENE-HEXENE MIXTURE BY SULFURIC ACID OF VARYING CONCENTRATIONS.

Expt. No.	Conc. of acid, % H_2SO_4.	Reaction temperature 0°.	Hours agitated.	Alcohol fraction of pptd. oil, %.	Unchanged hydrocarbons, %.	Loss as sulfuric esters and vaporization.	Polymers, %.
1.....	50	— 5°	2	1	90	1	8
2.....	75	0°	3	18	45	16	21
3.....	75	—10°	2	16	54	17	13
4.....	75	0°	2	10	67	9	14
5.....	75	0°	2.5	10	57	15	18
2 vol. acid							
6.....	75	—15°	2	10	70	12	8
7.....	85	—15°	2.5	22	32	14	32
8.....	85 + 1 vol. acetic acid	—10°	2.5	13	56	18	13
9.....	95	— 5°	2	4	5	11	75

When Expts. 2 and 4 are compared it will be seen that increased reaction time results in a larger yield of polymers and less alcohol.

From the work described above, it is obvious that large *losses* occur when highly cracked oils are treated with sulfuric acid in the usual manner and that the refined product *contains high boiling polymers*, and this too,

[1] *Ann.*, 190, 328 (1877).

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when the presence in gasoline of high boiling heavy oil, even kerosene, is commonly considered objectionable. The refining of cracked gasolines constitutes a special refining problem. The foul odor of cracked gasoline is however not due to olefins, but to sulfur compounds, nitrogen bases and traces of naphthenic acids, as we have previously pointed out. Diolefins are probably the cause of the resinification which has been observed when highly cracked gasolines are permitted to stand in storage for several months. We find that very sweet, stable gasolines may be made by treating with a small quantity, not over 6% by weight of 85 to 90% sulfuric acid, followed by washing with alkali in the usual manner and *redistilling*. This method of operating is sufficient to remove thoroughly the most reactive and objectionable constituents, *i. e.*, tar- or resin-forming diolefins and the malodorous compounds. Hall accomplishes the same object by distillation through Fullers earth, and Justice[1] seeks to attain the same result by milder polymerizing agents, *i. e.*, metallic chlorides such as zinc chloride or ferric chloride.

We believe, in the interest of conserving gasoline, the shortage of which will undoubtedly grow more acute, that the old sulfuric acid methods of refining should be discarded or modified, even if standards of quality heretofore the rule have to be modified and based solely upon efficiency during use.

The Presence of Alcohols in Petroleum "Acid Oils."—The odor of the highly aromatic fluid acid oils, regularly obtained as a refinery by-product, is mainly that of a mixture of secondary and tertiary alcohols derived from olefins, the amylenes to about duodecene, since the olefins above $C_{12}H_{24}$ in the series yield polymers almost exclusively. The odor of an artificial mixture made up of a number of these alcohols could not be distinguished from a sample of acid oil, washed neutral, from a petroleum refinery.

The actual demonstration of the presence of alcohols in acid oils obtained in refinery practice presented some difficulties owing to the large number of substances present, the wide range of distillation temperatures, the fact that the tertiary alcohols practically are not capable of acetylation or reaction with phthalic anhydride, etc. However, we had fair success by making use of the insolubility of the sodium alcoholates in a solution containing considerable dry ether. One kg. of light fluid acid oil recovered from the refining of cracked kerosene derived from a heavy Mexican crude petroleum was distilled with steam, thus obtaining about 750 g. as a light yellow highly aromatic oil, divided, as collected, into 3 fractions. This was thoroughly dried by fused potassium carbonate and diluted with an equal volume of dry ether. After adding sodium wire, the solution was gently boiled under a return condenser. The

[1] Eng. Pat. 3572, 1914; *J. Soc. Chem. Ind.*, 34, 1004 (1915).

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alcoholates were removed by filtering with suction, washed with dry ether and decomposed by water. The weight of the alcoholates totaled approximately 83 g. The odor of the alcohols strongly suggested the presence of secondary alcohols and in fact after acetylating with acetic anhydride, all three fractions possessed pleasant fruity ester odors. The saponification values however showed that a considerable portion had been converted into hydrocarbons. On attempting to distil a small portion of the first fraction to determine the boiling point range, decomposition with formation of water was observed. One gram of the acetylated last fraction, sp. gr. 0.912, showed a saponification number of 142, and since decyl acetate has the saponification number 280, it is apparent that considerable decomposition of the alcohols originally present occurred during acetylation.

From the alkaline aqueous solutions obtained as noted above, 5.5 g. of naphthenic acids were obtained. This naphthenic acid portion was converted into the methylester and then showed a boiling point above 225°, indicating more than 8 carbon atoms in the acids, and a saponification value of 246. The value calculated for $C_{10}H_{19}CO_2CH_3$ is 248. This close agreement may be only a coincidence and without particular significance. Sometime ago we isolated, in a similar manner, a small quantity of naphthenic acid from the gasoline fraction of this same Mexican petroleum, and the methylester had a saponification value of 516; calculated for $C_5H_9CO_2CH_3$ is 491. The odor of these naphthenic acids is very close to that of the Russian acids, but the naphthenic acids washed from Texas oils are heavy, viscous and nearly odorless.[1] Gurwitsch[2] has pointed out that naphthenic acids are removed by conc. sulfuric acid from petroleum oils to a degree of completion far in excess of any result which can be calculated on the basis of partition coefficients. Since the naphthenic acids of the Mexican and Texas oils have not been described and apparently not studied, we feel justified in thus briefly calling attention to their presence in these oils.

The Refining of Crude Benzols.—Crude benzols from coal-gas tar, carbureted water-gas tar, or "holder oil" and Pintsch gas "hydrocarbon drips" are noted for the relatively large per cent. of so-called unsaturated paraffins which they contain. After treating such benzols with sulfuric acid, and washing neutral with alkali, it is always noted that on redistilling the treated oil, large quantities of sulfur dioxide are evolved, accompanied by blackening of the still residues. These still residues are high-boiling viscous oils which on prolonged heating are convertible into pitch or resin, which some manufacturers erroneously designate as "coumarone

[1] In our opinion the practically odorless naphthenic acids from Texas oils merit consideration for many industrial applications in the form of their soaps.

[2] *Z. physik. Chem.*, **87**, 323 (1914); Zaloziecki, *Chem. Ztg.*, **16**, 905 (1892).

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resin." It is much more probable that they are highly polymerized products derived in part from cyclopentadiene and similar diolefin hydrocarbons.

The sulfur dioxide evolved during redistillation is derived from the decomposition of neutral sulfuric acid esters, the formation of which was noted above in the case of cracked gasolines. That the amount of sulfur dioxide evolved bears a certain relation to the relative amount of sulfuric acid employed in refining is shown in the following table. An increase in the specific gravity after refining may also be noticed.

TABLE V.—REFINING OF CRUDE BENZOLS WITH VARYING AMOUNTS OF SULFURIC ACID.

Kind of oil.	Ratio; vol. oil to acid.	$D_{4°}^{20°}$. Orig.	$D_{4°}^{20°}$. After treating.	G. SO_2 evolved per liter oil on redistillation.
Crude benzol.....	100:25	0.860	0.865	0.024
Crude benzol.....	100:12.5	0.860	0.865	0.364
Crude benzol.....	100: 7	0.860	0.866	0.480
Crude solvent naphtha ..	100:25	0.864	0.869	0.384
Crude solvent naphtha ..	100: 7	0.864	0.870	0.779
Crude benzol Pintsch....	100:12.5	0.845	0.880	0.751
Crude benzol Pintsch....	100: 7	0.845	0.882	2.064

Although the fact that high boiling residues are obtained by refining crude benzols rich in unsaturated hydrocarbons is more or less familiar to every one engaged in the practice, the common acceptance of the erroneous idea that the loss to conc. sulfuric acid is a measure of the volume per cent. of unsaturated aliphatic hydrocarbon present, makes it desirable to point out again that, as in the case of unsaturated gasolines, the polymerized hydrocarbons remain dissolved in the oil layer. The "loss" only respresents that portion of the unsaturated hydrocarbons which forms water-soluble sulfuric acid esters, alcohols, tar and loss by emulsion.

The following results were obtained by refining a crude benzol from carbureted water-gas tar.[1] It will be noted that the loss due to treating

[1] An interesting case has recently come to our notice, in which a manufactured lot of so-called C. P. benzol and C. P. toluol, made from carbureted water-gas tar, changed considerably on standing.

When freshly distilled, the benzol and toluol distilled from "first drop" to "dry point" well within the 2-degree limit commonly specified for these products. After storage for 4 months in clean metal drums, the distillation range was approximately 10°. A small part, not more than 1.5% of higher boiling oil was observed, although the first drop temperature was unchanged. This is due to the fact that part of the olefins originally present had escaped removal in the form of soluble sulfuric acid esters or by conversion into high boiling polymers, and had slowly polymerized, perhaps assisted by a trace of acid or metallic salts. Such deterioration is not noticed in the case of benzol and toluol made at high temperatures, as in by-product coke ovens, and relatively free from olefins, or even in benzol recovered from oil gas when the refining is carefully carried out with a much larger proportion of acid than is employed for good by-product benzol.

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with 0.1 volume of sulfuric acid is a little more than equalled by the % of high boiling polymers found in the residue boiling above 155°.

TABLE VI.

	I. Original crude benzol.	II. Product of refining I.
$D_{4°}^{20°}$	0.856	0.878
Distillation	%	%
To 75°	5.5	5.0
75– 85°	14.5	4.5
85– 95°	34.5	44.5
95–105°	19.0	13.8
105–115°	7.7	5.0
115–125°	3.8	2.5
125–135°	3.6	2.0
135–145°	3.5	1.8
145–155°	2.0	1.7
Residue	6.0	18.0
Loss on refining	10.2	..

Tars.—As pointed out above, none of the pure, unsaturated aliphatic hydrocarbons yield tars when treated with 85% or 94% sulfuric acid at 15°. With the crude benzols, however, containing as high as 85% benzol and its homologs, the development of heat on treating with conc. sulfuric acid is sometimes so great that it is difficult to control the temperature of the reaction mixture within this limit. This energetic reaction with sulfuric acid has been previously noted with certain diolefins, particularly the conjugated diolefins, and such hydrocarbons have been noted in crude benzols by Armstrong[1] and others.

We have noted tar formation with great liberation of heat, charring, etc., when treating the diolefins, myrcene and the diolefins made from linseed oil by destructive distillation of the calcium soap.

Cyclohexadiene[2] and cyclopentadiene[3] give tars instantly when treated with sulfuric acid. We believe the conclusion is warranted, therefore, that *the tars sometimes noted in refining gasolines and kerosenes made by "cracking" are due to the presence of diolefins*. Also, in view of the fact that the mono-unsaturated hydrocarbons, whose physical properties place them with the lubricating oils, *i. e.*, of about 24 or more carbon atoms, are much less reactive toward sulfuric acid than those of lower molecular weight proves that the *tars invariably obtained when crude lubricating oils are refined with sulfuric acid are not due to simple olefins*. The sludge tars from lubricating oil are formed from diolefines or perhaps other substances. Our knowledge of the real nature of the hydro-

[1] *J. Soc. Chem. Ind.*, 3, 462 (1884).

[2] Baeyer, *Ann.*, 278, 88 (1894).

[3] Kramer and Spilker, *Ber.*, 23, 3283 (1890); 29, 552 (1896).

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carbons, nitrogen bases, naphthenic acids, sulfur compounds, etc., occurring in crude lubricating oil distillates, is so extremely meager that almost nothing positive can be said as to the nature of these tars.

Quantitative Determination of Olefins.—According to the findings recorded in the present paper, together with other facts previously well established, it can be said that *at present there is no method for the quantitative determination of the per cent. by volume of unsaturated hydrocarbons in petroleum oils.* In the case of crude benzols, an approximation can be arrived at by thorough agitation with cold sulfuric acid, washing and neutralizing as usual, distilling and adding the amount of the polymerized heavy residue to the loss during refining. The volume of the heavy polymerized residue, plus the loss to the acid, equals approximately the volume per cent. of olefins originally present. The commercial practice of manufacturing C. P. benzol and toluol is substantially this series of operations. It is obvious that the chief source of error in such an analytical method lies in the fact that redistillation of a fraction collected up to a certain degree of temperature will always yield in a second distillation a small residue, boiling above the original upper limit of temperature. It is also obvious that any method for the separation of the unsaturated hydrocarbons which is based on solubility differences, must be exceedingly inaccurate. Thus the liquid sulfur dioxide refining method of Edeleanu employed, as an analytical method gives only very rough values, invariably too high in the case of gasolines and is not applicable at all to crude benzols or other distillates containing any considerable % of benzol hydrocarbons, owing to the great solubility of the aromatic hydrocarbons in this solvent.[1] As has been already pointed out, fuming sulfuric acid attacks saturated paraffin hydrocarbons to a very marked degree.

Although the method of determining unsaturated hydrocarbons, as originally proposed by Krämer and Böttcher, specified the employment of fuming sulfuric acid, the method as now usually described refers only to ordinary acid.[2]

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[1] Under the influence of light and heat, sulfur dioxide combines with olefins, forming hard, amorphous substances. Thus butylene forms a substance of the composition $(C_4H_8SO_2)_n$. Cf. Mathews and Elder, *J. Soc. Chem. Ind.*, **22**, 670 (1913).

[2] "The method consists in shaking 25 cc. of the crude petroleum with 25 cc. of sulfuric acid of the specific gravity 1.83, corresponding to ordinary strong sulfuric acid, about the equivalent of that used in petroleum refining. The acid and oil are shaken in a small flask with a long neck, the neck holding 25 cc. The flask is then filled with strong sulfuric acid until the oil which remains uncombined with the acid can be measured in the neck of the flask. The loss in volume between the original 25 cc. and the oil which remains undissolved by sulfuric acid is taken to represent the unsaturated hydrocarbons." Bacon and Hamor, "The American Petroleum Industry," I, 126.

Egloff in a recent paper on the analysis of light oils also employs 95% sulfuric

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[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY.]

ON THE SWELLING OF PROTEIN COLLOIDS.

A REPLY TO PROFESSOR MARTIN H. FISCHER.

BY LAWRENCE J. HENDERSON AND EDWIN J. COHN.

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Recently, in THIS JOURNAL, Professor Martin Fischer and his collaborators have returned to the problem of the swelling of colloids under the influence of solutions of varying acidity and alkalinity.[1] The results of these new investigations, though interpreted by Professor Fischer as favorable to his views upon the physico-chemical conditions of the distribution of water in colloidal systems, and upon the nature of edema, nephritis and uremia, and other pathological states, have hardly received from their authors the necessary quantitative mathematical analysis.

A casual inspection of the data of these papers shows that they prove, or rather confirm, the established fact that the necessary and sufficient condition for great swelling in such systems as Professor Fischer has studied is a high concentration of hydrogen or hydroxyl ions.

Further discussion of the results is rendered difficult by the fact that the authors have omitted to state the hydrogen-ion concentrations of their solutions. The abscissas of their geometrical diagram are merely the serial numbers assigned to their several experiments, while reference to the data shows that it is often impossible to estimate the concentration of ionized hydrogen in the solutions. Luckily, however, it is easy to calculate with sufficient accuracy this concentration in all cases where the values approach those that have been obtained for blood or for the other fluids of the organism (except gastric juice).

In Table I are assembled the data of Fischer and Hooker upon the swelling of gelatin plates in solutions of electrolytes where the hydrogen-ion concentrations even remotely approximate such concentrations as are known to occur within the organism, even in the most extreme pathological conditions. Whenever an accurate estimate is possible the values of these concentrations, expressed as p_H, are recorded.

Before considering the significance of the data below, it should be noted that the swelling of gelatin plates in pure water, as recorded among the data of these same experiments, indicates that a large variation in the ex-

acid to determine the olefins. His plan of analysis, however, is directed only to the final determination of the % of aromatic hydrocarbons present, which is really determined by the final fractional distillation of the refined and steam rectified oil. Egloff does not in any way indicate that the high boiling residues contained in the refined oil are in large part derived from polymerization of lower boiling olefins. *Met. Chem. Eng.*, 17, 262 (1917).

[1] Fischer and Hooker, THIS JOURNAL, 40, 272 (1918); Fischer and Benzinger, *Ibid.*, p. 292; Fischer and Coffman, *Ibid.*, p. 303.

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TABLE I.—DATA OF FISCHER AND HOOKER.

A. Phosphate Mixtures.

Ratio.	$\frac{NaH_2PO_4}{Na_2HPO_4}$ →	10:0.	8:2	6:4	4:6	2:8	0:10
Approximate	pH →	?	6.3	6.7	7.0	7.4	?
Experiment IV.....	24 hours	7.42	8.21	8.44	8.50	8.90	8.61
	48 hours	8.28	9.31	9.49	9.56	10.05	9.85
Experiment V.....	18 hours	5.15	7.65	8.00	8.42	8.55	8.48
	42 hours	6.88	9.14	9.80	10.24	10.50	10.31
Experiment VI.....	22 hours	6.28	7.00	7.50	7.90	8.16	8.68
	45 hours	7.10	8.03	9.14	9.09	9.30	10.06
Experiment VII.....	20 hours	5.90	7.11	7.65	7.50	8.02	8.17
	44 hours	6.78	8.44	9.00	9.00	9.45	9.70
Experiment VIII....	20 hours	7.10	8.68	9.35	9.49	9.81	10.23
	44 hours	8.27	10.27	11.16	11.31	11.57	12.14
Mean, 33 hours		6.92	8.38	8.95	9.10	9.43	9.62

B. Citrate Mixtures.

Ratio.	$\frac{\text{Disodium citrate}}{\text{Trisodium citrate}}$ →	10:0	8:2	6:4	4:6	2:8	0:10
Approximate	pH →	?	5.1	5.3	5.6	6.0	?
Experiment XIII....	24 hours	8.02	8.05	8.22	8.26	8.19	8.16
	48 hours	8.93	8.96	8.80	9.23	9.34	9.03
	72 hours	9.46	9.50	9.48	10.02	9.54	9.41
Mean, 48 hours		8.80	8.84	8.83	9.17	9.02	8.87

The data represent gain in parts of one part gelatin.

tent of the swelling of parallel experiments is to be expected. This may be illustrated by the data for the swelling in 24 hours, that period of time which yields the most satisfactory agreement.

TABLE II.

Experiment.	I	II.	III.	IV	X.	XI.	XII.	XIII.
Swelling.....	7.60	7.41	6.52	6.86	5.94	5.92	5.98	6.35

A comparison of these two tables shows that near the neutral point there is at most a very small change in the swelling of gelatin plates accompanying changes in the concentration of acid and base in the solution, or in union with the protein. Such changes as seem to be indicated by the data in question involve a slight diminution in swelling with increasing acidity or diminishing alkalinity. This conclusion also merely confirms the results of previous experiments.[1]

The experiments of Fischer and Benzinger on the swelling of fibrin also agree with previous observations upon the same subject.

Professor Fischer is therefore confronted with the situation that his latest experiments, when clearly stated, fully confirm the facts that have been employed by others to controvert his theoretical conclusions. If we may quote his own words, "Irrespective of the manner in which these

[1] Cf. Henderson, Palmer and Newburgh, *J. Pharmacol.*, 5, 449 (1914).

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mixtures are prepared (whether by progressive substitution of one salt for another, through the addition of the requisite acid to an alkali, through the addition of alkali to the proper acid, or through the addition of either acid or alkali to a given salt) it is found, when amount of water is plotted on the vertical and change in composition of the mixture on the horizontal" that for such conditions as are known to occur in the body the curve is approximately a horizontal straight line.

It is from these experiments that Professor Fischer now draws the following conclusions: "These findings are held to be applicable to the problem of water absorption by protoplasm and to sustain the old contention that even in the presence of buffer salts, there is an increase in water absorption (increased turgor or edema) with every increase in the acid (or alkali) content of the protein colloids found in the involved cell, organ or organism."

But the findings do in fact show that in the presence of the buffer mixtures of protoplasms, which alone are relevant to the question, there is little or no change in water absorption with change in the acid (or alkali)

TABLE III.—CONCENTRATION CELL MEASUREMENTS ON SOLUTIONS OF HYDROCHLORIC ACID CONTAINING GLUTENIN.

Experiment number.	Concentration of HCl.	Concentration of NaCl.	Concentration of glutenin.	$\frac{C_{HCl}}{C_{glutenin}}$.	pH.
520	0.0050 N	0	0.5%	10	2.56
531	0.0100	0	1.0	10	2.54
533	0.0100	0	1.0	10	2.60
533	0.0100	0	1.0	10	2.40
520	0.0050	0	1.0	5	3.05
527	0.0050	0.009 N	1.0	5	3.05
533	0.0050	0	1.0	5	3.05
533	0.0050	0	1.0	5	2.88
527	0.0033	0.009	1.0	3.3	3.39
531	0.0033	0.009	1.0	3.3	3.50
513	0.0030	0.001	1.0	3.0	3.37
533	0.0030	0	1.0	3.0	3.50
533	0.0030	0	1.0	3.0	3.40
520	0.0100	0	4.0	2.5	3.83
520	0.0050	0	2.0	2.5	3.78
533	0.0020	0	1.0	2.0	3.85
533	0.0020	0	1.0	2.0	3.77
513	0.0020	0.0015	1.0	2.0	3.82
514	0.003	0.001	2.0	1.50	3.99
520	0.0050	0	4.0	1.25	4.48
533	0.0010	0	1.0	1.00	4.43
533	0.0010	0	1.0	1.00	4.86
533	0.0010	0	1.0	1.00	4.67
520	0.0025	0	4.0	0.625	5.17
514	0.0010	0.002	2.0	0.5	5.14

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content of the protein colloids. Not until Professor Fischer has found a colloid unlike gelatin in this respect can he hope to maintain this part of his argument.

The question of the entrance of acid into the gelatine plates involves another problem. But these experiments also support the view that the acid or alkali content of the protein colloids is a function of the hydrogen ion concentration of the solution, a theory which has perhaps never been doubted by any one but Professor Fischer. It is of course true that the method of preparation of the protein, the concentration and nature of the electrolytes in the solution, and a variety of other factors, must somewhat influence the heterogeneous equilibrium, and might conceivably influence it greatly. This, however, is a question which can only be investigated experimentally. Fischer's data point to no such large effect. The preceding unpublished data of our own upon the equilibrium between a very pure preparation of glutenin and hydrochloric acid also strongly indicate that the hydrogen-ion concentration of the solution is the important factor in determining the amount of acid taken up by the protein.

These results are reported graphically upon the accompanying diagram. The fact that the ratio of acid to protein plotted against the values of p_H yields a smooth curve may be regarded as an indication that the protein behaves like the solution of a polyvalent base, acid, or amphoteric substance.

From Fischer's own data, from those above reported, which bear more directly upon the problem, and from the known facts concerning the isohydric points of proteins, it seems certain that, as a rule, the amount of acid or base combined with most simple proteins within the physiological or pathological ranges of reaction are low and liable to little variation. Not until Fischer has found in the tissues sufficient quantities of proteins of a quite different avidity for bases or acids, can he maintain this part of his argument.

It is in vain that Professor Fischer seeks to establish a simple account of such diseases as nephritis, or such conditions as edema and uremia. No doubt simple conditions are involved in these complex conditions, but there is at present no way of conceiving them simply, except by shutting the eyes to the facts. Fischer has completely failed to establish his thesis, because it is well known that acidosis is a variable phenomenon in these conditions, and also in many others which are not contemplated by his theory.

Finally, it is simply not permissable to disregard the accurate quantitative measurements which have been accumulated in many laboratories of biological chemistry, of physiology, and of clinical medicine during the last decade. On the basis of Fischer's speculations the theory of the regulation of breathing, one of the most splendid achievements of modern physiology, which has stood the test of aviation, of gas warfare, and of

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military medicine, is almost meaningless. Yet it is a fact that the composition of the blood determines the activity of the respiratory centre so as to adjust the hydrogen-ion concentration of the blood at a constant point.[1] This is only one of many facts which Professor Fischer has always disregarded.

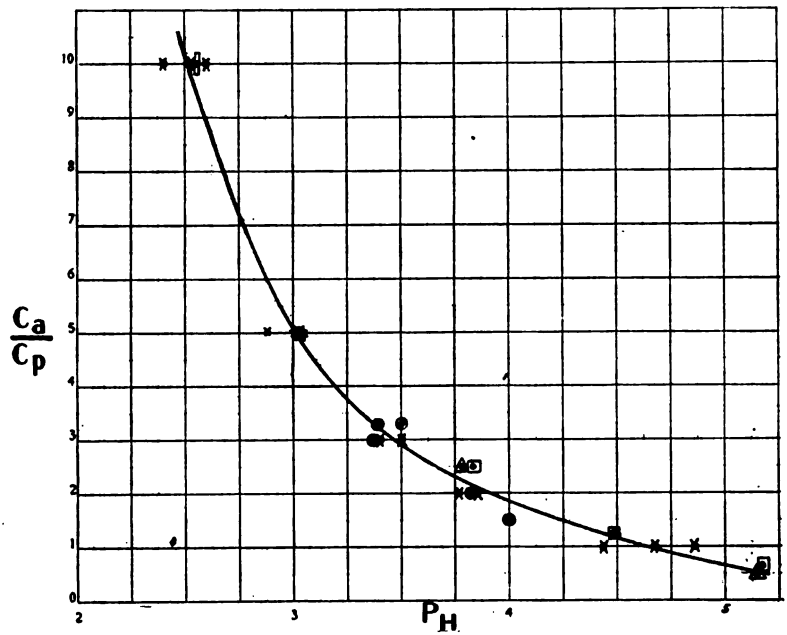

Fig. 1.—Concentration cell measurement on solutions of hydrochloric acid containing glutenin.

$\frac{C_a}{C_p}$ = Ratio of normal concentration of acid to per cent. concentration of protein.

P_H = log C_H.

0.5% glutenin; 1.0% glutenin; 1.0% glutenin containing salt; 2.0% glutenin; 4.0% glutenin.

Questions of this kind, however, are not merely of scientific interest, for medical practice is also involved. Therefore in view of the above discussion, we feel bound once more to protest against therapeutic measures founded upon theories which are often inconsistent with, and always unsupported by, the established facts of chemistry and physiology.

CAMBRIDGE, MASS.

[1] Cf. Haldane, "Organism and Environment as Illustrated by the Physiology of Breathing," New Haven, 1917; and Barcroft, "The Respiratory Function of the Blood," Cambridge, England, 1914.

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[CONTRIBUTION FROM THE EICHBERG LABORATORY OF PHYSIOLOGY IN THE UNIVERSITY OF CINCINNATI.]

THE COLLOIDAL-CHEMICAL THEORY OF WATER ABSORPTION BY PROTOPLASM.

A FIFTH RESPONSE TO SOME CRITICISMS.

BY MARTIN H. FISCHER.

Received March 5, 1918.

The Editor and Professor Lawrence J. Henderson have kindly permitted me to see the preceding article in manuscript form and to make reply.[1]

To avoid misunderstanding I shall in the following quote directly those pieces of Henderson's latest article which possess sufficient body to make response possible.

Henderson opens as follows:

"Recently ..... Fischer and his collaborators have returned to the problem of the swelling of colloids under the influence of solutions of varying acidity and alkalinity."

I have in all my writings scrupulously avoided the use of just such terms as "acidity" or "alkalinity," employing such non-committal terms as "acid or alkali content" just because the terms "acidity" and "alkalinity" are variously defined by different authors (in terms of titration value by the old school, or in terms of hydrogen- or hydroxyl-ion concentration by the modern physical chemists) and because, as I have so many times insisted upon before, the effects of acids and of alkalies nowhere parallel either of these acidities or alkalinities either in the physiological behavior of tissues (like their water absorption) or in such simple processes as the absorption of water by protein colloids.

Henderson continues:

"A casual inspection of the data of these papers shows that they rather confirm the established fact that the necessary and sufficient condition for great swelling in such systems is the high concentration of hydrogen or hydroxyl ions."

It all depends upon what one means by "great" swelling or "high" concentration. In the papers under criticism, as well as in my older studies, it is shown that simple proteins in the presence of acids or alkalies may easily absorb a hundred times (10,000%) their dry weight of water. It must be clearly understood, however, that no such degrees of swelling are ever necessary to account either for the normal amounts of water held by cells or tissues or the excessive amounts which they may contain in even extreme grades of edema. The greatest edema that I have ever been able to produce *experimentally* in an *isolated* organ amounted to less than

[1] See also the previous criticisms of L. J. Henderson and his co-workers, *J. Biol. Chem.*, 13, 404 (1913); *Arch. Int. Med.*, 12, 146, 163 (1913); *J. Pharmacol.*, 5, 449, 466 (1914); answer may be found to these in my "Edema and Nephritis," 2nd Ed., 633, 650, New York, 1915.

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250% of the moist weight of the tissue. No such edemas can, however, be produced in whole animals and have the animals live. A maximum obtainable in frogs was 60% and extreme grades of edema in human beings rarely run above 25% of the normal weight of the individual. Such edemas moreover can be tolerated only in the extremities or in organs where swelling goes on unhampered by capsules or bony outer structures. An edema of the brain amounting to an increase in weight of but 5% leads to stupor, and an edema of this organ amounting to 8% results in death.

I introduce these figures because Henderson's criticisms would lead one to believe that something approximating the first figures would have to be obtained in order to explain the swelling characteristic of various "diseases" (nephritis, glaucoma, "uremia," edema of the brain, etc.) instead of the lowest figures.

How easily the biologically necessary per cents. may be covered by a slight shifting in the acid or alkali content of the tissues may be seen from Henderson's own revision of my experimental findings as put together in Table I of his paper. I pass over certain obvious objections which may be launched against this method of his, such as his ignoring of concentration of the phosphate mixtures, his working in averages, etc. In spite of this, his rearrangement of my tables does not obscure the fact that with changes in the acid or alkali content of the mixtures there is an increase in swelling amounting from a few per cent. to 50% of the moist weight of the gelatin—enough, therefore, to cover even the extremes of water absorption observed in clinical cases of edema, and this within the realm of those changing "hydrogen-ion acidities" which Henderson himself acknowledges as "physiological."

Henderson continues:

"It should be noted that the swelling of gelatin plates in pure water .....indicates that a large variation in the extent of the swelling of parallel experiments is to be expected."

This is an attempt to discredit the significance of the increased swelling observed in Henderson's admittedly "physiological" or "neutral" zone. But, as every colloid chemist knows, these differences are largely temperature effects and are taken into account in every series of experiments by employing in each of such series one or more water controls as blanks.

Henderson writes:

"A comparison of these two tables shows that near the neutral point there is at most a very small change in the swelling of gelatin plates accompanying changes in the concentration of acid and base in the solution, or in union with the protein."

As noted above this "very small change" may amount to 50%.

"Professor Fischer is, therefore, confronted with the situation that his latest experiments.....fully confirm the facts.....employed by others, to controvert his theoretical conclusions."

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And with the same amount of compulsion.

Henderson next inserts some perfectly correct quotations from my papers which need no comment. He continues:

"But the findings do in fact show that in the presence of the buffer mixtures of protoplasm, which alone are relevant to the question, there is little or no change in water absorption with change in the acid (or alkali) content of the protein colloids."

Only several to 50%.

"The question of the entrance of acid into the gelatin plates involves another problem. But these experiments also support the view that the acid or alkali content of the protein colloids is a function of the hydrogen-ion concentration of the solution, a theory which has perhaps never been doubted by anyone but Professor Fischer."

I have never denied that in the entrance of acid into gelatin, in the question of the acid content of a protein and, I might add, in the problem of water absorption by protein or protoplasm the concentration of the hydrogen ions is *a* function of the process. I have always maintained, and do now, that it is not the *only* function.

Henderson next writes:

"It is of course true that the method of preparation of the protein, the concentration and nature of the electrolytes in the solution, and a variety of other factors, must somewhat influence the heterogeneous equilibrium, and might conceivably influence it greatly."

Very true, as my studies show. The "heterogeneous equilibrium" may be so violently influenced that the function of the hydrogen ions is obscured entirely. The order in which hydrochloric, lactic and sulfuric acids influence protein swelling or water absorption by tissues decreases in the sequence in which they are named, in spite of the fact that the hydrogen-ion concentration is high in the dilute aqueous solutions of the first and last acids and low in the lactic. In fact, lactic acid is almost as powerful in this regard as hydrochloric, while fibrin and other proteins swell little more in sulfuric acid than in distilled water. To these items may be added that, no matter what the concentration of any acid, addition of any neutral salt decreases the amount of the protein swelling, and this out of all proportion to any fancied decrease in hydrogen-ion acidity brought about through the added salt.

Henderson adds:

"This, however, is a question which can only be investigated experimentally. Fischer's data point to no such large effect."

See the preceding paragraph, or any of the score of papers or books that I have published on this subject.[1]

[1] Martin H. Fischer, "Physiology of Alimentation," New York, 1907; "On the Swelling of Fibrin (with Gertrude Moore), *Am. J. Physiol.*, **20**, 330 (1907); "The Nature and Cause of Oedema," *J. Am. Med. Assoc.*, **52**, 830 (1908); "Ueber die Analogie zwischen der Wasserabsorption durch Fibrin und durch Muskel," Pflüger's *Arch. für Physiol.*,

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Henderson continues:

"The following unpublished data of our own upon the equilibrium between a very pure preparation of glutenin and hydrochloric acid also strongly indicate that the hydrogen-ion concentration of the solution is the important factor in determining the amount of acid taken up by the protein."

No doubt this is true but the point under discussion is not the acid taken up by a protein, but the *water*.

"These results are reported graphically upon the accompanying diagram. The fact that the ratio of acid to protein plotted against the values of p_H yields a smooth curve may be regarded as an indication that the protein behaves like the solution of a polyvalent base, acid, or amphoteric substance."

124, 69 (1908); "Weitere Versuche über die Quellung des Fibrins," *Ibid.*, **125**, 99 (1908); "Ueber Augenquellung und das Wesen des Glaucoms," *Ibid.*, **125**, 396 (1908); "Ueber Augenquellung und das Wesen des Glaucoms," *Ibid.*, **127**, 1 (1909); "Ueber Hornhauttrübungen," *Ibid.*, **127**, 46 (1909); "Bemerkungen zu einer kolloidchemischen Theorie des Lackfarbwerdens der roten Blutkorperchen," *Kolloid-Z.*, **5**, 146 (1909); "Ueber die Antagonistische wirkung der Neutralsalze auf die Quellung des Fibrins in Säuren und Alkalien" (with Gertrude Moore), *Ibid.*, **5**, 197 (1909); "Ueber die Entstehung und Natur des Stauungsoedem der Niere und der Leber" (with Gertrude Moore), *Ibid.*, **5**, 286 (1909); "The Relief of Glaucoma through Subconjunctival Injections of Sodium Citrate" (with Hayward G. Thomas), *Ann. Ophthalm.*, **19**, 40 (1910); "Das Oedem als kolloidchemischen Problem (nebst Bemerkungen über die allgemeine Natur der Wasserbindung in Organismen)," *Kolloidchem. Beihefte*, **1**, 93 (1910); "Ueber das Wesen der Trüben Schwellung," *Kolloid-Z.*, **8**, 159 (1911); "Weiteres zur Kolloidchemischen Analyse der Nephritis," *Ibid.*, **8**, 201 (1911); "On the Nature, Cause and Relief of Glaucoma," *Trans. Am. Acad. Ophthalm. Oto-laryng.*, 193 (1911); "Beiträge zur Kolloidchemischen Analyze der Absorptions und Secretionsvorgänge" (Die Absorption aus der Bauchhöhle), *Kolloidchem. Beihefte*, **2**, 304 (1911); "Zur Theorie und Praxis der Transfusion" (with James J. Hogan), *Ibid.*, **3**, 385 (1912); "Ueber die Konktraktilität von Katgut und die Theorie der Muskelkontraktilität" (with W. H. Strietmann), *Kolloid-Z.*, **10**, 65 (1912); "Ueber die Aufnahme von Wasser durch das Nervengewebe" (with M. O. Hooker), *Ibid.*, **10**, 283 (1912); "A Response to Some Criticisms of the Colloid-Chemical Theory of Water Absorption by Protoplasm," *Biochem. Bull.*, **1**, 444 (1912); "Further Remarks on the Treatment of Nephritis," *Trans. Assoc. Am. Phys.*, **27**, 595 (1912); "A Further Response to Some Criticisms of the Colloid-Chemical Theory of Water Absorption by Protoplasm," *J. Am. Med. Assoc.*, **59**, 1429 (1912); "The Colloid-Chemical Theory of Water Absorption by Protoplasm" (a third response to some criticisms), *Ibid.*, **60**, 348 (1913); "The Treatment of Nephritis and Allied Conditions," *Ibid.*, **60**, 1682 (1913); "Weitere Beiträge zur Behandlung der Nephritis und verwandter Erscheinungen," *Kolloidchem. Beihefte*, **4**, 343 (1913); "Some Physicochemical Principles in Therapy," *Forchheimer's Therapeusis of Internal Diseases*, **1**, 1, New York (1913); "On the Colloid-Chemical Action of the Diuretic Salts" (with Anne Sykes), *Science*, **37**, 845 (1913); "Non-Electrolytes and the Colloid-Chemical Theory of Water Absorption" (with Anne Sykes), *Science*, **38**, 486 (1913); "Ueber die kolloid-chemische Wirkung der diuretischen Salze" (with Anne Sykes), *Kolloid-Z.*, **13**, 112 (1913); "Ueber den Einfluss einiger Nichtelektrolyte auf die Quellung von Protein" (with Anne Sykes), *Ibid.*, **14**, 215 (1914); "Ueber die Kolloidchemie der Zuckerdiurese" (with Anne Sykes), *Ibid.*, **14**, 223 (1914); etc., etc. For a running account, see my "Edema and Nephritis," 2nd Ed., New York, 1915.

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Also true, but what connection does Henderson expect to have made of this, with the problem of water absorption?

".....it seems certain that, as a rule, the amount of acid or base combined with most simple proteins within the physiological or pathological ranges of reaction are low and liable to little variation."

But even these "low" amounts are sufficient to account for very considerable edemas. The increased carbonic acid content of venous blood over arterial raises the "hydrogen-ion acidity" but little, yet even this is sufficient to increase the water absorption by the cells in the blood stream 5 to 15%, and if there is any interference with the free circulation of the blood, the figure jumps to 30%.[1]

"Finally, it is simply not permissable to disregard the accurate quantitative measurements which have been accumulated in many laboratories of biological chemistry, of physiology, and of clinical medicine during the last decade."

Certainly not! Not even when done in my laboratory.

"On the basis of Fischer's speculations the theory of the regulation of breathing, one of the most splendid achievements of modern physiology, which has stood the test of aviation, of gas warfare, and of military medicine, is almost meaningless."

Why so? I happen to have admired and taught the principles established by Haldane and his followers for years past.

"Yet it is a fact that the composition of the blood determines the activity of the respiratory center so as to adjust the hydrogen-ion concentration of the blood at a constant point."

This is only partially true and then only for normal individuals as Haldane and the English clinicians have themselves shown. In cases of heart disease, respiratory disease, diabetes and other clinical conditions associated with edema the observations of these very authors show that evidences of an abnormally high acid content of the blood and tissues (as evidenced, among other things, by an abnormally high hydrogen-ion acidity of the blood) are regularly present.

".....in view of the above discussion, we feel bound once more to protest against therapeutic measures founded upon theories which are often inconsistent with, and always unsupported by, the established facts of chemistry and physiology."

This is Henderson's opinion. Among those of another persuasion in this matter of therapy are Arthur D. Dunn,[2] Albert J. Bell,[3] Paul G. Woolley,[4] Edgar G. Ballenger and Omar F. Elder,[5] Rufus Southworth,[6] Gordon F.

[1] See H. J. Hamburger, *Osmotischer Druck and Ionenlehre*, 1, 291, 404, Wiesbaden, 1902.

[2] Arthur D. Dunn, *Lancet-Clinic*, 108, 8 (1912).

[3] Albert J. Bell, *Am. J. Med. Sci.*, 144, 669 (1912); personal communication (1914).

[4] Paul G. Woolley, *J. Am. Med. Assoc.*, 63, 596 (1914).

[5] Edgar G. Ballenger and Omar F. Elder, *J. Am. Med. Assoc.*, 62, 197 (1914).

[6] Rufus Southworth, *Lancet-Clinic*, Sept. 5 (1914).

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McKim,[1] H. Lowenburg,[2] Geo. T. Grinnan,[3] H. B. Weiss,[4] J. Mitchell Clarke,[5] Herbert Brown,[6] W. deB. MacNider,[7] A. W. Sellards,[8] V. Pleth[9] and many more.

CINCINNATI, OHIO.

ON THE SWELLING OF PROTEIN COLLOIDS. A REPLY.

BY L. J. HENDERSON.

Received March 5, 1918.

Professor Fischer's rejoinder seems to me to call for no modification of my original statement. But, in that he has at length undertaken to consider the question of the quantitative relation between change of volume of a colloid and change of hydrogen-ion concentration, I wish to make the following additional remarks:

First, Fischer is mistaken in supposing that I have admitted or that there is in fact any evidence that the hydrogen-ion concentration in any part of the body can ever vary as widely as in those solutions of his to which attention has been called. The present state of knowledge upon variations of the hydrogen-ion concentration in the body may be illustrated by Michaelis's extensive studies of venous blood.[10] The data fall into three groups: (I) 64 measurements on 28 normal specimens; (II) 34 measurements on 17 pathological specimens from cases of diabetes, nephritis, and edema, which therefore involve conditions contemplated by Fischer's theories; (III) 38 measurements on 19 pathological specimens representing various other diseases. The data are summarized in the following table:

TABLE I.—VALUES OF p_H FOR VENOUS BLOOD (MICHAELIS).

	I.	II.	III.
High	7.67	7.67	7.74
Low	7.49	7.50	7.42
Mean	7.58	7.58	7.62
Range	0.18	0.17	0.32

Evidently the values of p_H for venous blood, both in normal and in pathological conditions, are liable to very small variations. In a single case of diabetic coma just before death Michaelis observed a value of p_H of 7.12.

[1] Gordon F. McKim, personal communication (1914).

[2] H. Lowenburg, *J. Am. Med. Assoc.*, **63**, 1906 (1914).

[3] Geo. T. Grinnan, *Virg. Med. Semi-Month.*, **20**, 523 (1916).

[4] H. B. Weiss, *J. Am. Med. Assoc.*, **68**, 1618 (1917); *Ohio State Med. J.*, **13**, 595 (1917).

[5] J. Mitchell Clarke, *Brit. Med. J.*, **2**, 239 (1917).

[6] Herbert Brown, personal communication from Flanders received Sept. 1, 1917.

[7] W. deB. MacNider, *J. Exp. Med.*, **23**, 171 (1916); *Ibid.*, **26**, 19 (1917); *Proc. Soc. Exp. Biol. Med.*, **14**, 140 (1917).

[8] A. W. Sellards, "Acidosis and Clinical Methods," Cambridge, 1917.

[9] V. Pleth, personal communication, 1917.

[10] L. Michaelis, "Die Wasserstoffionenkonzentration," Berlin, 1914, pp. 101–105.

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Such observations are the sole evidence that the normal reactions of the blood can suffer substantial change, even for a few hours.

Secondly, according to Fischer's measurements, these variations of p_H which Michaelis has observed in the venous blood of nephritics, diabetics, etc., involve a change of swelling of gelatin plates of less than 2%. Fischer's estimate of a 50% change of volume is therefore illusory and his further remarks are irrelevant.

Professor Fischer must demonstrate very much wider variations of hydrogen-ion concentration than are now known to occur within the organism or very much greater changes in swelling within physiological ranges than are now known, before there can be any ground for accepting his theories.

This is not the place to enter upon a discussion of the physiology of respiration or the changes in volume of the blood corpuscles. But in order to avoid misunderstandings I venture to say that Fischer's interpretations of both phenomena seem to me contrary to the evidence.[1]

CAMBRIDGE, MASS.

NOTES.

Rapid Organic Combustions of Substances Containing Nitrogen.—In a note "On Rapid Organic Combustions"[2] the use of cerium dioxide as a catalyst deposited on asbestos was supplemented by cupric oxide, and it was shown that by the addition of the lead peroxide-minium mixture the method could be used for determining carbon and hydrogen in substances containing nitrogen also. The lead peroxide which was obtained by us was found to be very unsatisfactory, and this same trouble was mentioned recently by Wise in connection with the micro method.[3] At first we abandoned the use of the lead peroxide altogether, and by keeping the latter part of the cupric oxide at a comparatively low temperature some fair results were obtained. When, however, a very active catalyst was used a large amount of nitric acid was formed and in one series of experiments the tube, after 8 runs, was finally completely clogged on account of the formation of a basic copper nitrate. The lead peroxide mixture is usually placed about 5 cm. beyond the cupric oxide and must be kept at about 300–320°[4] in order to avoid the decomposition of any lead nitrate formed.[5] The

[1] Cf. Haldane, J. S., "Organism and Environment as Illustrated by the Physiology of Breathing," New Haven, 1917; Barcroft, J., "The Respiratory Function of the Blood," Cambridge (England), 1914; Höber, R., "Physikalische Chemie der Zelle und der Gewebe," Leipzig, 1914.

[2] Reimer, THIS JOURNAL, **37**, 1636 (1915).

[3] Wise, *Ibid.*, **39**, 2055 (1917).

[4] Dennstedt, "Anleitung zur vereinfachten Elementaranalyse," III Aufl., p. 66, Hamburg, 1910.

[5] Lead nitrate decomposes rapidly at 357°. Baekeland, THIS JOURNAL, **26**, 391 (1904); Morgan, *J. Phys. Chem.*, **8**, 416 (1904). We could not find any specific data on the temperature of decomposition of the basic copper nitrates.

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adjacent cupric oxide, therefore, is sometimes kept at a temperature which is not high enough to decompose the nitrate of copper that might be formed. This seems to be a serious objection in general to the use of cupric oxide in addition to the catalyst if it is expected that *several* combustions of substances containing nitrogen are to be made *unless* care is taken to make sure that any nitrate of copper is completely decomposed after each combustion by proper heating, by the entire renewal of the cupric oxide, or by extending the distance between the cupric oxide and the lead peroxide mixture so that *all* the cupric oxide can be heated to a dull red heat.

In our experiments the cerium dioxide was deposited on pumice of 12-mesh size. This has the advantage over asbestos in that the material then does not crumble and "sag."[1]

HARRY L. FISHER AND A. H. WRIGHT.

LABORATORY OF ORGANIC CHEMISTRY,
COLUMBIA UNIVERSITY.

Organic Chemicals Available at the University of Illinois.—During the past eight months a large number of organic chemicals, not available in the open market, have been manufactured at the University of Illinois. As the demand has been great, it has been impossible to keep many of them in stock at all times and at present not more than one-half of those that have been made are on hand.

This summer it is planned to have a staff of chemists extend the work, manufacturing not only the chemicals previously made but also still others for which the demand may be urgent. If it is possible to know beforehand the approximate amount of each compound that may be desired, great saving of time will result and the selling prices of the chemicals will be lowered. This note is written to urge laboratories which may be interested in any of the compounds mentioned below to write as soon as possible for quotations so that the raw materials in the correct amounts may be purchased without delay. Below are given three lists. First, chemicals now available in amounts from a few grams to 10 or more pounds. Second, substances for which the processes have been worked out but which are not in stock at the present time. Third, substances which it is hoped may be synthesized this coming summer. Quotations will gladly be given on any of the chemicals in Groups I and II, and in Group III a maximum price will be quoted wherever feasible.

If there are any substances not included in these lists which are badly needed by any technical or university laboratory, the manufacture of such will be considered, provided the preparations are not too long and difficult, and provided the demand is sufficient to warrant the labor involved.

[1] Since the above was written the excellent article "On Rapid Organic Combustions" by Levene and Bieber, THIS JOURNAL, 40, 460 (1918) was published. In conversations with one of us, Prof. Reimer and Dr. Levene also urged the publication of the above.

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Group I.—Chemicals Now Available.

Acetyl bromide
Amylene
Anisol
Benzamide
Benzanilide
Benzenesulfonyl chloride
Benzilic acid
Benzil
Benzoin
Benzoyl chloride
Benzyl bromide
Benzyl cyanide
Bromoacetyl bromide
α-Bromonaphthalene
Butyl alcohol (normal)
o-Bromotoluene
p-Bromotoluene
Caprylic alcohol
Chloroacetic anhydride
Chloroacetyl chloride
Chlorocarbonic ester (ethyl)
Chloropicrin
o-Chlorotoluene
p-Chlorotoluene
p-Dibromobenzene
Dichlorohydrin
Dimethylglyoxime
Diphenylcarbamine chloride
Diphenyl ether
Epichlorohydrin
Ethyl iodide
Fluorescein
Furfurol
Glycol
Glycol diacetate
Hippuric acid
Iodine monobromide
β-Iodopropionic acid
Isoamyl bromide
Isoamyl ether
Isobutyl aldehyde
Magnesium, for Grignard
Malic acid
Malonic ester (ethyl)
Mesitylene
Methylamine hydrochloride
Methylethyl ketone
Methylene iodide
Methyl oxalate
p-Nitrobenzoic acid
Nitromethane
Oxalyl chloride
Piperidine
Salicylic aldehyde
Sodium nitroprusside
Tetranitromethane
Thionyl chloride
Trimethylene bromide
Trimethylene glycol

Group II.—Chemicals Which Will Be Available but Are Not Now in Stock.

Acetamide
Acetonitrile
o-Acetotoluid
p-Acetotoluid
Allyl alcohol
Allyl bromide
Azobenzene
Benzophenone
Benzoyl bromide
p-Bromoacetanilide
p-Bromoaniline
o-Bromobenzoic acid
p-Bromobenzoic acid
p-Bromophenol
Chinaldine
p-Chloraniline
o-Chlorobenzoic acid
p-Chlorobenzoic acid
Cupferron
Cyanacetic ester (ethyl)
Diethylmalonic ester (ethyl)
Dimethylamine hydrochloride
Dimethylaminobenzaldehyde
Ethyl oxalate
Glycocoll
Malonic ester (methyl)
Mercury dimethyl
Methyl iodide
Nitroso β-naphthol
Phenylacetic acid
Phenylacetic ester (ethyl)
Phenylalanine
Phenylisocyanate
Phloroglucin
Quinone
Thiophenol
Trimethylenechlorohydrin

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GROUP III.—CHEMICALS WHICH WILL PROBABLY BE PREPARED DURING THE SUMMER.

Acetylene tetrabromide
Benzenesulfonamide
Benzylamine
Butyl aldehyde (normal)
Butyl bromide (normal)
Diethylamine
Diphenylhydrazine
Ethylamine hydrochloride
Formamide
Iodobenzene
Methylphenyl hydrazine
α-Naphthyl hydrazine
Naphthyl isocyanate
Ninhydrin
o-Nitrobenzaldehyde
m-Nitrobenzaldehyde
p-Nitrobenzaldehyde
p-Nitrobenzoyl chloride
Nitron
p-Nitrophenyl hydrazine
Oenanthol
Oenanthylic acid
p-Thiocresol
Triethylamine
Trimethylamine hydrochloride
Urethane
m-Xylene
o-Xylene
p-Xylene

Inquiries should be addressed as soon as possible to the Organic Chemical Division, University of Illinois.

ROGER ADAMS.

URBANA, ILLINOIS.

NEW BOOK.

Notions Fondementales de Chimie Organique. Par CHARLES MOUREAU. Member de l'Institut et de l'Académie de Médecine, Professeur au College de France. Cinquieme edition revue et consideralblement augmentée. Paris: Gauthier-Villars, 1917. 20 Fr. VIII—548 pp.

The fourth edition of this book was published in 1913 and reviewed in THIS JOURNAL, **36**, 1064. The fifth edition has been revised and increased by 165 pages.

The book is divided into five sections: I, Introduction and General Theories, 159 pages; II, Hydrocarbons, 54 pages; III, Oxygen Compounds, 166 pages; IV, Nitrogen Compounds, 70 pages; V, Organic-metallic Compounds, 5 pages; VI, Heterocyclic Compounds, 18 pages; VII, Dyes, 39 pages.

The method of treatment is rather radically different from that adopted in American and English text-books for beginners. In the introduction the author considers in detail the molecular and atomic theories, isomerism, valence, stereochemistry, optical activity, physical properties and the mechanism of reactions. The aim of the book seems to be to present general principles first and concrete examples later and rather sparingly. It is, perhaps, worth our while to enquire whether such a method has not considerable advantage from the pedagogical point of view and whether in our attempt to give facts first and theory later it does not sometimes happen that our students fail to see the forest because of the trees.

The numerous, brief historical references with dates are very welcome. In some cases the emphasis ought, perhaps, to be a little different, but

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in view of the author's evident intention to be impartial and of his request for corrections, criticisms here would be out of place.

The hypothesis of "active" and "inactive" molecules to explain the velocity of chemical reactions, after the analogy of the hypothesis of Arrhenius which preceded the ionic theory, is interesting, but every one must see that the hypothesis in its present form is very vague and indefinite. It is something, however, to recognize, as Professor Moureau does, that there is something about which we need further knowledge. Too many are satisfied with differential equations without enquiring what lies back of them.

The author follows Berthelot in considering the terms "spontaneous" and "forced," applied to reactions, as synonymous with "exothermic" and "endothermic;" if a constant temperature of 1000° is maintained, the reaction between carbon and steam goes on just as "spontaneously" and reaches an equilibrium just as truly as the reaction between hydrogen and oxygen. To call one reaction "forced" and the other "spontaneous" does not help us at all to understand why heat is absorbed in one case and given out in the other. Instead of that, it tends to conceal the fact that there is something here about which we are badly in need of further knowledge. The real distinction is, of course, between reactions having available "free energy" and those which do not.

The chapter on dyes is excellent and will be very useful at the present time. The logical arrangement of the material—hydrocarbons, oxygen compounds, nitrogen compounds, etc., is well suited to the author's treatment and well adapted to give students a clear view of the relations which must be mastered in securing a knowledge of organic chemistry.

W. A. Noyes.

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[CONTRIBUTION FROM THE ANALYTICAL LABORATORY, DEPARTMENT OF CUSTOMS, OTTAWA.]

THE ACIDIMETRY OF COLORED SOLUTIONS: AN APPLICATION OF THE POCKET SPECTROSCOPE.

BY ALFRED TINGLE.

Received January 9, 1918.

Introduction.

In the course of certain work carried on at this laboratory, it was necessary to titrate alkaloidal solutions containing much coloring matter. The latter, as frequently happens in such cases, could not be removed without vitiating the quantitative results. The method of overcoming this trouble, proposed by A. H. Allen, could not be applied. Allen dissolved the base and impurities in a solvent immiscible with water, then added standard acid until methyl orange in the aqueous layer showed an acid reaction. The natural coloring matters with which the writer had to deal passed into the aqueous layer to an extent sufficient to mask any available indicator. This does not appear to be a novel experience.

The spectroscope seemed to offer a means of differentiating the color produced by an indicator from that produced by colored resins. It also appeared probable that the change of color of an indicator at the neutral point could be as readily determined by the spectroscope as by the naked eye.

On the whole, the results have justified this belief, though it has been

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found that certain precautions are necessary which were not foreseen at the outset of the work. The conditions of success have been worked out for 5 indicators. There seems no reason to suppose that the same cannot be done for all. In this work a large spectroscope is neither necessary nor desirable. The results here recorded were obtained with a small "Beck-Thorp" Direct Vision Diffraction instrument, which can be carried in the pocket. Very likely an instrument of the older-fashioned direct vision prism type would have been just as serviceable.

Method of Conducting Titrations.

A blank experiment is necessary to fix the end-point of most indicators. It was found that, as a general rule, where the breadth of an absorption band is changed by the solution becoming alkaline, the change is progressive and increases with the alkalinity. Thus the position of the edge of the band will be determined by the concentration of the indicator, the thickness of liquid through which the light passes, and the degree of alkalinity of the solution.

The titrations may be made in any convenient vessel. Its shape is unimportant so long as it and the spectroscope are so placed that the same thickness of liquid is viewed after each addition of alkali. The writer has often used conical flasks for the purpose. Most of the experiments recorded here were made in flat-sided tincture bottles.

Two similar titration vessels must be provided. The first contains the liquid to be titrated, brought to such dilution that a sufficient amount of light can pass through it.[1] In the second vessel, used for the "blank," is placed nearly the same volume of water (some excess being allowed for the standard solution which will be added), made alkaline by one drop of decinormal sodium hydroxide solution. The indicator which is to be used is added slowly from a buret or a Mohr's pipet to this faintly alkaline solution till it is seen that the edges of the absorption bands are sufficiently well defined. The position of the most characteristic edge of the most characteristic band is registered on the scale (or by the luminous pointer in the Beck-Thorp instrument). This defines the end-point of the titration. The volume of indicator solution used must also be noted. The same volume of indicator solution is next added to the acid liquid to be titrated, and standard alkali is then run in as usual until the position of the characteristic absorption band is seen to be that registered from the "blank" as the end-point. The only difference from an ordinary titration lies in the fact that between every two additions of alkali the liquid should be examined spectroscopically instead of by the naked eye.

[1] If, for any reason, dilution is not permissible and the liquid is very dark, special vessels must be employed so that only a very thin layer of solution is under examination.

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Should the end-point be overrun, back titration can always be employed, so long as the end is eventually obtained by adding alkali to an acid solution and not *vice versa*.

It may be here noted that, in general, very much larger quantities of indicator are needed in this method than would be desirable in ordinary titrations.

The Degree of Accuracy Obtained.

This point was tested after taking every precaution to eliminate the effects of unconscious personal bias from the experimental results.

Separate portions of decinormal sulfuric acid were measured carefully, diluted, and colored with a carefully neutralized vegetable extract to such extent that an "end-point" could not be distinguished by the unaided eye. They were then handed to the experimenter, who was not aware of the amount of acid present until the titrations had been completed.[1] The coloring matter used was in some cases prepared from tea and in others from stick licorice. It seems unnecessary to give details of the means used to insure neutrality. The solutions were titrated against an approximately decinormal solution of sodium hydroxide which had been standardized in the usual manner. The titrations were made in flat-

TABLE I.—TITRATIONS WITH DIFFERENT INDICATORS.

Expt. No.	Volume of 0.1 N H_2SO_4 by direct measurement. Cc.	Volume of 0.1 N H_2SO_4 calculated from titration results. Cc.	Difference. Cc.	Indicator.	Volume of indicator solution used in titration. Cc.	Strength of indicator solution.
1.....	15.0	15.21	+0.21	Cochineal	2.5	Saturated in 50% alcohol
2.....	26.0	25.98	—0.02	Cochineal	2.5	
3.....	20.0	19.96	—0.04	Cochineal	2.5	
4.....	21.0	21.04	+0.04	Methyl orange	1.0	0.1%
5.....	17.5	17.49	—0.01	Methyl orange	1.0	0.1%
6.....	18.5	19.16	+0.66	Methyl orange	1.0	0.1%
7.....	14.0	14.11	+0.11	Methyl orange	1.0	0.1%
8.....	22.5	22.43	—0.07	Methyl orange	1.0	0.1%
9.....	20.3	20.15	—0.15	Lacmoid	0.4	0.2%
10.....	21.5	21.73	+0.23	Lacmoid	0.4	0.2%
11.....	18.7	18.97	+0.27	Lacmoid	0.4	0.2%
12.....	15.0	14.90	—0.10	Phenolphthalein	0.2	1.0%
13.....	20.3	20.28	—0.02	Phenolphthalein	0.2	1.0%
14.....	16.5	16.34	—0.16	Phenolphthalein	0.2	1.0%
15.....	21.8	21.73	—0.07	Rosolic acid	0.2	1.0%
16.....	15.1	15.13	+0.03	Rosolic acid	0.2	1.0%
17.....	15.4	15.51	+0.11	Rosolic acid	0.2	1.0%

The bad result obtained in Expt. 6 is attributed to a sudden irregularity which developed in the artificial light used as a source of the bright spectrum.

[1] The author's thanks are due to Mr. F. W. Babington, Chief Analyst in this laboratory, who very kindly measured out these acids for him and who helped in many other ways to bring this work to a speedy and successful issue. His kindly help and encouragement in this as in other cases has been invaluable.

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sided tincture bottles. All solutions were diluted to approximately 50 cc. at the outset, the thickness of liquid through which the observations were made being nearly 45 mm. Some of the experiments were made by daylight, and others at night under such conditions that the "end-point" could not have been seen, even had no coloring matter been present.

Lacmoid is, from the nature of its absorption spectrum, the most difficult indicator to use in this fashion.

In judging the above results it must be remembered that the method is intended for use in cases where the liquid to be titrated is so colored that no other means can be used for detecting the end-point, or where the operation must be performed under adverse conditions as to light. Apart from such conditions it is only in connection with methyl orange that the writer would suggest the use of the spectroscope instead of the unaided eye. The work involved in the new method is greater, because even the most handy instrument is not as quick in action as the eye itself.

In all the foregoing experiments on colored solutions the coloring matter used was such that absorption due to it was confined to the blue end of the spectrum. The method can be equally well applied when absorption is at the red end.

An example of the latter sort is supplied by solutions of copper salts. The determination of sulfuric acid in the presence of copper sulfate is an operation of technical importance, *e. g.*, in control of electro-deposition baths. As commonly carried out, it is very difficult to determine the correct end-point. Spectroscopic determination of this point is very easy.

To a solution of 2.5 g. of pure crystallized copper sulfate in 40 cc. of water, 25 cc. of decinormal sulfuric acid was added. The mixture was then titrated against sodium hydroxide solutions, using methyl orange as an indicator. The spectroscope showed that neutrality was reached on adding 26.2 cc. of alkali.

A subsequent titration of 25 cc. of the same acid alone, using lacmoid as indicator, showed that 26.2 cc. of the same alkali solution was needed for neutrality.

With the spectroscope there was no difficulty in finding the end-point, which was almost, or quite, indistinguishable without it.

A saturated solution of copper sulfate diluted 6 times is sufficiently transparent to be used in this method in a layer 45 mm. thick, the illumination being only moderate.

Characteristics of the Indicators.

Before using this method of titration the analyst should acquaint himself by experience with the peculiarities of the selected indicator.

The following remarks may guide him and save waste of time, but each

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person must decide for himself the working conditions which best suit his circumstances. No attempt has been made in this work to characterize the absorption bands in any numerical way, for their breadth varies with several factors. In the experiments on which these remarks are based, the volume of liquid to which the indicators were added was approximately 70 cc. and the thickness through which the spectra were observed was 40–45 mm. Little attention has been paid to the changes in the edges of the absorption bands nearest the violet end of the spectrum for two reasons: (1) This edge, in the case of most of the bands examined, is not so sharply defined as the other. (2) Much of the violet and blue is absorbed by the brown and yellow natural coloring matters which are usually responsible for obscuring the end-point in this class of titration.

Cochineal.—The indicator solution was of such strength as could be obtained by allowing 50% alcohol to extract as much pigment as possible from an excess of cochineal powder.

When 2.5 cc. of such a solution is added to the standard volume of acidified liquid, absorption does not extend much beyond the blue region of the spectrum, but on neutralization the band extends over almost the whole of the green region and acquires a sharper edge. The neutral point must be determined in a carefully made blank experiment, for the change in color is progressive with increasing alkalinity. It is well known that an excess of alkali changes the color of cochineal; spectroscopically observed, this change is marked by an extension of the absorption towards the red. In a properly managed titration, taking the precautions mentioned, the end-point can be readily detected.

Methyl Orange. Neutral.—This is used in 0.1% solution. The commercial article is weighed, moistened with dil. hydrochloric acid and evaporated to dryness. The product is moistened with dil. ammonium hydroxide in excess and again evaporated until completely dry, dissolved in water and diluted to the required volume. In this way neutrality is secured. The directions usually given for preparing this indicator result in the presence of free acid. When 1 cc. of the above solutions is added to the standard volume of water a sharp enough edge is produced at the end of the absorption band nearest to the red. This band covers part of the green and much of the blue region of the spectrum. Addition of alkali produces no change, but acidification causes the band to move towards the red end until, when all the indicator has been converted into free acid, it covers practically the whole green region. At the same time the absorption becomes sharper.

Neutral methyl orange as thus prepared and used in this large quantity is only intended for use in titrations when an alkali is being added to an acid. Used *vice versa*, an error would be introduced to the amount of the standard acid required to acidify the indicator,

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The fact that the spectrum of neutral methyl orange does not differ from that of an alkaline solution shows that the common practice of carrying titrations in which it is used to "the intermediate tint" is a mistaken one. The correct end-point has not been reached until no further color change is produced.

In a recent paper with F. W. Babington,[1] the present author made some comments on the discrepancy observed between the titers of alkali solutions as determined by different indicators. It has now been shown that, as far as methyl orange is concerned, the discrepancy arises from "the intermediate tint" being considered the sign of neutrality.

That the discrepancy does not occur when the spectroscopic end-point is taken is shown by the results tabulated below. In the experiments from which they are derived only the usual amount of indicator was added when the end-point was observed by the eye alone. The solutions used were not in any way colored except by the indicator.

TABLE II.—END POINTS.

Titration of 25.0 cc. of 0.1 N H_2SO_4 with NaOH.

Indicator.	Eye alone. Cc. required.	Using spectroscope. Cc. required.
Methyl orange	25.2	25.3
Cochineal	25.3	25.3
Lacmoid	25.3	..

Lacmoid.—The strength of the stock solution used in these experiments was 0.2%. Under the standard conditions it was found that 0.4 cc. was needed to produce the characteristic spectroscopic effect. At this concentration the visible spectrum transmitted consists only of red rays when the reaction is acid. When neutral these also are absorbed, blue being transmitted if the source of light is sufficiently powerful. Under normal conditions, however, neutrality is indicated by total suppression of the whole spectrum. The spectroscopic end-point with this reagent is not very sharp. Probably improvement could be effected by using a more dilute stock solution. This would make it possible to regulate more closely the depth of color suitable to each titration.

Phenolphthalein.—A 1% stock solution was used. For each experiment 0.2 cc. was taken, but the exact amount does not affect the position of the absorption bands to be observed, as is the case with most other indicators. This is because the change taking place when the end-point is reached consists in the development of a totally new band in the green, closely bordering upon the yellow region, one edge almost coinciding with the "D line."

Rosolic Acid.—The stock solution was 1%, and of this 0.2 cc. was a convenient amount to take for titrations made under these standard con-

[1] *Chemical Industry in Canada during the War*, **10**, 32; *J. Soc. Chem. Ind.*, **36**, 1203–4 (1917) (abs.).

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ditions. When the solution becomes very slightly alkaline the absorption band which is characteristic of the acid solution broadens abruptly, extending further into the green towards the red end of the spectrum, but leaving some of the green region still visible. The indications are very marked, so that rosolic acid lends itself well to this spectroscopic method. The neutral point as indicated by the spectroscope is the same as that found without its aid, so that the divergence of indications by rosolic acid from those by other indicators is not eliminated by the use of this new method.

Litmus and Hematoxylin have been examined only as to their suitability for use with the spectroscope in a very cursory manner, but the probabilities appear to be in their favor. Litmus must be used in considerably larger quantity than usual, as in the case of cochineal and methyl orange. When alkaline, it shows a well marked band. Hematoxylin gives a sharply defined edge to the absorption band seen in alkaline solution only when a considerable amount of it is present.

Summary.

1. The spectroscope is an efficient means of distinguishing the exact neutral point in many acidimetric titrations.

2. It can be used for this purpose in cases where the unaided eye would fail.

3. The necessary concentration of most indicators is greater when they are to be used in connection with the spectroscope.

4. The best conditions under which some of the commonest indicators can be used in connection with the spectroscope have been established.

OTTAWA, CANADA.

ON EQUILIBRIUM IN THE SYSTEM: FERROUS CARBONATE, CARBON DIOXIDE AND WATER.[1]

BY HERBERT J. SMITH.

Received January 18, 1918.

It has long been known that ferrous carbonate is more soluble in water containing carbon dioxide than in pure water.[2] The increase in solubility is due to the formation of the more soluble ferrous bicarbonate, which has, however, never been obtained in the solid state. It is shown in this paper that the solid salt, at a temperature of 25°, would have a decomposition tension of carbon dioxide greater than 25 atmospheres.

If we study the system: ferrous carbonate, carbon dioxide and water

[1] From a dissertation submitted to the Faculty of the Ogden Graduate School of Science of the University of Chicago in candidacy for the Degree of Doctor of Philosophy.

[2] Wagner, *Z. anal. Chem.*, 6, 171 (1867); Hauer, *J. prakt. Chem.*, 81, 381 (1860).

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from the standpoint of the ionic theory and the law of mass action, we find that a certain quantitative relation must exist between the concentration of the dissolved ferrous salt and concentration of the carbon dioxide in solution.

The following 5 equations govern the equilibrium:

$$[H^+] \times [HCO_3^-] = K_1 \times [H_2CO_3] \quad (1)$$

$$[H^+] \times [CO_3^{--}] = K_2 \times [HCO_3^-] \quad (2)$$

$$[Fe^{++}] \times [CO_3^{--}] = K_3 \text{ (The solubility product constant)} \quad (3)$$

$$[HCO_3^-] = 2[Fe^{++}] \quad (4)$$

$$\alpha \times [Fe(HCO_3)_2] = [Fe^{++}] \quad (5)$$

where α is the degree of ionization of the ferrous bicarbonates.

Dividing Equations 1 by 2 we get

$$\frac{[HCO_3^-]^2}{[CO_3^{--}]} = \frac{K_1}{K_2} \times [H_2CO_3]. \quad (6)$$

Multiplying (6) by (3) we have

$$[HCO_3^-]^2 \times [Fe^{++}] = \frac{K_1K_3}{K_2} [H_2CO_3]. \quad (7)$$

But since from (4) $2[Fe^{++}] = [HCO_3^-]$ we have

$$\frac{[Fe^{++}]}{\sqrt[3]{[H_2CO_3]}} = \sqrt[3]{\frac{K_1K_3}{4K_2}} \text{ and since } [Fe^{++}] = \alpha \times [Fe(HCO_3)_2], \quad (8)$$

we have finally

$$\frac{\alpha \times [Fe(HCO_3)_2]}{\sqrt[3]{[H_2CO_3]}} = \sqrt[3]{\frac{K_1K_3}{4K_2}} = K \quad (9)$$

where K is the equilibrium constant for the system.

No quantitative data can be found in the literature for testing the applicability of Equation 9. However, Stieglitz[1] and McCoy and Smith[2] have applied a similar expression to measurements on the solubility of calcium carbonate in carbonated waters, and have shown that a good equilibrium constant is thereby obtained.

In Table I are given the results of some experiments which I have carried out on equilibrium in the system: ferrous carbonate, carbon dioxide and water.

The ferrous carbonate used was prepared according to the following method: Equimolecular quantities of solid ferrous sulfate and sodium bicarbonate were placed in a steel bottle. The air was displaced from the bottle by a stream of carbon dioxide. Water previously saturated with carbon dioxide was added. The bottle was then closed by a plug carrying a needle valve and carbon dioxide was added from a cylinder of compressed gas until a pressure of 400 pounds had been attained in

[1] *Carnegie Inst. Publication*, 107, 233 (1909).

[2] THIS JOURNAL, 33, 468 (1911).

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the bottle. The valve was then closed, and the bottle kept at a temperature of 100° for several days. The ferrous carbonate obtained in this way is pure white.

The precipitate was filtered in an atmosphere of carbon dioxide and washed with water previously saturated with the gas. The precipitate is much more easily filtered and washed than one obtained by precipitation in open vessels. According to Senarmont[1] the crystals obtained by the above procedure are isomorphous with calcite and similar to the mineral siderite.

From 50 to 100 g. of the ferrous carbonate were placed in the steel bottle described by McCoy and Smith.[2] One liter of water was added, and carbon dioxide admitted through the needle valve from a cylinder of the liquefied gas. A pressure gauge afforded a means for determining the approximate pressure of the gas within the bottle. The bottle was rotated in a thermostat at 30° for several days until a state of equilibrium had been reached. Preliminary experiments showed that one week's rotation was sufficient for this.

When equilibrium had been finally attained within the bottle, the concentrations of the dissolved ferrous salt and of the carbon dioxide in solution were determined. The portion of the solution used for the analysis was withdrawn from the bottle through a brass tube packed with cotton. This tube was attached to the valve on the inside of the bottle. For the carbon dioxide determination the filtered portion was received in a tared and evacuated flask containing a few cc. of conc. sulfuric acid. The gas was removed from the flask by a stream of carbon dioxide-free air, and dried by passing through conc. sulfuric acid and over phosphorus pentoxide. It was finally absorbed in weighed Fleming towers filled with soda-lime and phosphorus pentoxide. It will be noted that in this way all of the carbon dioxide, both free and combined, is evolved. Since the iron exists in solution as the bicarbonate, the free carbon dioxide is easily obtained by subtracting from the total twice the concentration of the iron. All concentrations must be expressed, of course, in gram molecules per liter. The portion used for the iron analysis was boiled with nitric acid to oxidize the iron. The iron was next precipitated as ferric hydroxide, the precipitate washed with boiling water and redissolved in dil. sulfuric acid. The iron was then reduced to the ferrous state, using amalgamated zinc. Finally, the iron was determined by titration with seventieth normal potassium permanganate.

In the first column of Table I are given the concentrations of free carbonic acid in gram molecules per liter. The second column gives the corresponding concentrations of the ferrous bicarbonate in gram

[1] *Compt. rend.*, 28, 693 (1849).

[2] THIS JOURNAL, 33, 468 (1911).

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molecules per liter. The third column gives the assumed degrees of ionizations of the ferrous bicarbonate. These ionizations I have assumed to be the same as for barium nitrate solutions of equivalent concentrations. The ionization values for barium nitrate are those given by Noyes and Melcher.[1] In the fourth column are given values for K, the equilibrium constant for the system. These values are obtained from Equation 9, using the data in Cols. 1, 2 and 3 of the table.

TABLE I.—SOLUBILITY OF FERROUS BICARBONATE IN CARBONATED WATER AT 30°.

1. (H_2CO_3).	2. $Fe(HCO_3)_2$.	3. α.	4. $K \times 10^3$.
0.1868	0.00245	0.912	3.91
0.1985	0.00256	0.909	3.99
0.2168	0.00262	0.908	3.96
0.2327	0.00274	0.907	4.04
0.2960	0.00303	0.902	4.10
0.3116	0.00304	0.902	4.04
0.3153	0.00318	0.898	4.19
0.3294	0.00311	0.900	4.05
0.3745	0.00315	0.898	3.93
0.4046	0.00332	0.896	4.02
0.4750	0.00348	0.893	3.98
0.6600	0.00402	0.884	4.08
0.7154	0.00418	0.880	4.11
0.7600	0.00434	0.878	4.18
		Av.,	4.04

Rearrangement of Equation 9 gives

$$[Fe^{++}] \times [CO_3^{--}] = K_3 = \frac{4K_2K^3}{K_1}. \qquad (10)$$

We see that, given the values of K_1 and K_2, we can calculate the value of K_3, since K is now known.

The value of K_1, the first ionization constant of carbonic acid, was first accurately determined by Walker and Carmack.[2] They found K_1 to equal 3.04×10^{-7} at 18°. A more recent, and perhaps a slightly more accurate, value has been obtained by Kendall.[3] He found K_1 to equal 3.12×10^{-7} at 18°. Kendall also determined values for K_1 at 0° and at 25°. Assuming that the value increases at the same rate between 25 and 30° as it does between 0 and 25°, we get a value for K_1 of 3.75×10^{-7} at 30°.

The best value for K_2, the second ionization constant for carbonic acid, has been obtained by Seyler and Lloyd.[4] The calculation of K_2 from their experimental data involves a knowledge of K_1 and of K_w (ion product

[1] *Carnegie Inst. Publication*, 63, 108 (1907).
[2] *J. Chem. Soc.*, 77, 8 (1900).
[3] THIS JOURNAL, 38, 1480 (1916).
[4] *J. Chem. Soc.*, 111, 138 (1917).

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constant for water). Using Kendall's value for K_1 at 25° and taking K_w equal to 0.82×10^{-14}, they obtained 4.91×10^{-11} as the value of K_2 at 25°. No experimental data are known from which the variation of K_2 with temperature can be determined.

If, in Equation 10 we substitute 3.75×10^{-7} for K_1; 4.91×10^{-11} for K_2; and 4.04×10^{-3} for K, we get K_3 equal to 34.53×10^{-12}. Then if ferrous carbonate were not hydrolytically dissociated, its solubility in pure water free from carbon dioxide would be 5.8×10^{-6} gram molecules per liter.

AGRICULTURAL COLLEGE, MISSISSIPPI.

ON EQUILIBRIUM IN THE SYSTEM: ZINC CARBONATE, CARBON DIOXIDE AND WATER.[1]

BY HERBERT J. SMITH.

Received January 18, 1918.

When zinc salts in solution are precipitated by alkaline carbonates, the compounds produced are apparently unstable and of variable composition. A large number of basic zinc carbonates have been described in the literature. It has been shown, however, by Mikusch[2] that there exist only 2 carbonates of zinc. One is the normal zinc carbonate, $ZnCO_3$; the other is a basic zinc carbonate whose composition is expressed by the formula $5ZnO.2CO_2.4H_2O$. All other basic zinc carbonates described in the literature are shown to be solid solutions of zinc hydroxide and neutral zinc carbonate.

It has been shown by Free[3] that the solubility of basic copper carbonate increases with the concentration of free carbon dioxide. Seyler[4] points out that Free's results exhibit regularities similar to those found for other carbonates. Seyler deduces these regularities from the principles of chemical equilibrium and shows experimentally that they apply to the solubility of basic zinc and lead carbonates. No previous experimenters have examined the equilibrium between normal zinc carbonate, carbon dioxide, and water for pressures of carbon dioxide greater than one atmosphere. In view of this fact, I have undertaken a study of this system under high pressures.

The theory of this equilibrium from the standpoint of the law of mass action and the ionic theory is similar to that deduced for the system: ferrous carbonate, carbon dioxide and water. This is given in the preceding paper. Since the valence of zinc ion is the same as that of the fer-

[1] From a dissertation submitted to the Faculty of the Ogden Graduate School of Science of the University of Chicago in candidacy for the Degree of Doctor of Philosophy.

[2] *Z. Phys. Chem.*, **56**, 367 (1906).

[3] THIS JOURNAL, **30**, 1366 (1908).

[4] *Analyst*, **33**, 756 (1908).

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rous ion, an equation similar to (9) of that paper should hold for the zinc equilibrium.

The zinc carbonate used in these experiments was prepared from the purest commercially obtainable zinc carbonate by washing repeatedly with large quantities of boiling water. The basic zinc carbonate thus obtained was placed with water in a steel bottle and carbon dioxide was added until a pressure of 30 atmospheres was reached. The steel bottle was rotated in a thermostat at 25° for several days.

About 50 g. of the zinc carbonate thus prepared was placed in a steel bottle. The bottle was then nearly filled with water and closed with a plug carrying a needle valve, through which it was charged with carbon dioxide from a cylinder of the liquefied gas. The inside of the bottle was protected from the action of the carbonic acid by a coating of beeswax applied hot. The cylinder and bottle were then rotated in a thermostat for several days until equilibrium had been reached. Preliminary experiments showed that about one week's rotation was necessary for this.

The solution was then analyzed for dissolved zinc salt and carbon dioxide. In this case the zinc was determined by adding to a weighed portion of the solution an excess of 0.05 *N* hydrochloric acid, boiling to remove all carbon dioxide, cooling, adding one drop of methyl orange, and titrating the excess of acid with 0.05 *N* barium hydroxide. This method of analysis is described by Kantor and Benedikt.[1] Preliminary experiments carried out with known weights of zinc showed it to be accurate. The carbon dioxide was determined as described in the accompanying paper on ferrous carbonate.

In Table I are given the results of experiments carried out at 25°. Table II gives results at a temperature of 30°. Col. 1 gives concentration of free carbonic acid in gram molecules per liter. Col. 2 the concentrations of zinc bicarbonate in gram molecules per liter. Col. 3 gives the degrees of ionization of the zinc bicarbonate. It is assumed that the bicarbonate is ionized to the same extent as zinc chloride solutions of equivalent concentrations. The ionization of the zinc chloride solutions are calculated from the data given in Kohlrausch's *Leitervermögen der Elektrolyte*, 1st Edition, p. 160 (1898). Col. 4 gives the values of the equilibrium constant calculated from the equation

$$\frac{\alpha \times [Zn(HCO_3)_2]^2}{\sqrt[3]{[H_2CO]}} = \sqrt[3]{\frac{K_1K_2}{4K_3}} = K.$$

In the fifth column are given the pressures of the carbon dioxide. These pressures were not actually measured, but were calculated on the assumption that Henry's law holds for high pressures of the gas. The solubility of the gas in pure water at 25° under one atmosphere is given by Geffcken[2]

[1] *Z. angew. Chem.*, 1888, p. 236.

[2] Geffcken, *Z. phys. Chem.*, 49, 273 (1904).

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as 0.03374 gram molecules per liter. However, these calculated pressures are lower than the actual pressures, as it is well known that Henry's law does not apply under these high pressures.

TABLE I.—SOLUBILITY OF ZINC CARBONATE IN CARBONATED WATER AT 25°.

1. $[H_2CO_3]$.	2. $[Zn(HCO_3)_2]$.	3. α.	4. $K \times 10^3$.	5. Atmospheres pressure.
0.1390	0.00194	0.909	3.40	4.12
0.1797	0.00211	0.905	3.39	5.33
0.2579	0.00242	0.899	3.41	7.64
0.3580	0.00270	0.894	3.40	10.61
0.4103	0.00278	0.894	3.35	12.16
0.4480	0.00291	0.892	3.39	13.29
0.6657	0.00317	0.888	3.22	19.73
0.6969	0.00319	0.888	3.20	20.65
0.7610	0.00343	0.885	3.33	22.56
1.3701	0.00445	0.871	3.48	40.61
			Av., 3.36	

TABLE II.—SOLUBILITY OF ZINC CARBONATE IN CARBONATED WATER AT 30°.

1. $[H_2CO_3]$.	2. $[Zn(HCO_3)_2]$.	3. α.	4. $K \times 10^3$.
0.1838	0.00215	0.904	3.42
0.3838	0.00277	0.894	3.41
0.4038	0.00286	0.892	3.41
0.4601	0.00308	0.889	3.55
0.6064	0.00324	0.888	3.40
0.6257	0.00337	0.886	3.49
0.7470	0.00352	0.884	3.43
0.8351	0.00376	0.880	3.51
1.0840	0.00339	0.878	3.41
1.1275	0.00429	0.874	3.60
			Av., 3.47

Since $$K = \sqrt[3]{\frac{K_1K_2}{4K_3}} \quad \text{or} \quad K_3 = \frac{K^3.K_{42}}{K_1}$$

it is possible to calculate K_3, the solubility product constant of zinc carbonate. Substituting $K = 3.36 \times 10^{-3}$, $K_1 = 3.50 \times 10^{-7}$ and $K_2 = 4.91 \times 10^{-11}$, we find $K_3 = 21 \times 10^{-12}$ at 25°.

If zinc carbonate were not hydrolytically dissociated, its solubility in pure water at 25° would be 4.58×10^{-6} gram molecules per liter.

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COLLOIDAL PHENOMENA AND THE ADSORPTION FORMULA.

By John A. and Wynnaretta H. Wilson.

Received January 31, 1918.

The theory of the molecular mechanism of protein swelling recently presented by Tolman and Stearn[1] stands out in marked contrast to that evolved by Procter and Wilson.[2] According to the former, the force causing swelling is one of electrostatic repulsion, while in the latter theory this force is ascribed to the diffusion pressure of the necessary excess concentration of diffusible ions of the jelly phase over that of the external solution. Grounds for discussion have been furnished and the importance of the subject demands the attention of physical chemists in general. While this work is of great biological importance, it also has an enormous bearing upon the application of modern science to industry. It is not our purpose in the present paper to criticize the work of Tolman and Stearn, but rather to summarize briefly and to extend the theory of Procter and Wilson and to examine the widely-accepted, empirical formula for adsorption, as regards its reliability as a criterion of physical phenomena.

The Consequence of Chemical Combination between a Binary Electrolyte[3] and a Colloid Jelly.

Let us consider a purely hypothetical substance G which has the following properties: It is a colloid jelly, is completely permeable to water and all dissolved electrolytes, is elastic and under all conditions under consideration follows Hooke's law, and combines chemically with the positive, but not the negative ion of a binary electrolyte $M\,N$, according to the equation

$$[G] \times [M^+] = K[GM^+]. \qquad (1)$$

(In other words, the compound GMN is completely ionized into GM^+ and N^-.)

Now take one millimole of G and immerse it in an aqueous solution of MN. The solution penetrates G, which thereupon combines with some of the positive ions, removing them from solution, and consequently the solution within the jelly will have a greater concentration of N^- than of M^+, while in the external solution $[M^+]$ is necessarily equal to $[N^-]$. The solution thus becomes separated into 2 phases, that within and that surrounding the jelly, and the ions of one phase must finally reach equilibrium with those of the other phase.

At equilibrium, in the external solution, let

$$x = [M^+] = [N^-]$$

and in the jelly phase let

[1] This Journal, 40, 264 (1918).

[2] *J. Chem. Soc.*, 109, 307 (1916).

[3] Meaning exclusively an electrolyte which dissociates into two monovalent ions.

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$$y = [M^+]$$

and

$$z = [GM^+]$$

whence

$$[N^-] = y + z.$$

(All concentrations are taken in moles per liter.)

The relation existing between the concentrations of diffusible ions of the 2 phases at equilibrium can be derived from the consideration of the transfer of an infinitesimally small amount, dn moles, of M^+ and N^- from the outer solution to the jelly phase, in which case, since no work is actually done,

$$dn\ RT \log x/y + dn\ RT \log x/(y + z) = 0,$$

whence

$$x^2 = y(y + z). \qquad (2)$$

But in this equation, the product of *equals* is equated to the product of *unequals*, from which it follows that the sum of those unequals is greater than the sum of the equals, *i. e.*,

$$2y + z > 2x.$$

This is a mathematical proof that the concentration of diffusible ions of the jelly phase is greater than that of the external solution and makes possible the derivation of a second equation involving e, which is defined as the excess of concentration of diffusible ions of the jelly phase over that of the external solution

$$2x + e = 2y + z. \qquad (3)$$

Since $[N^-]$ is greater in the jelly than in the surrounding solution, the negative ions of the colloid compound will tend to diffuse outward into the external solution, but this they cannot do without dragging their colloid cations with them. On the other hand, the cohesive forces of the elastic jelly will resist this outward pull, the quantitative measure of which is e, and according to Hooke's law

$$e = CV \qquad (4)$$

where C is a constant and V the increase in volume in cubic centimeters of one millimole of the colloid.

Now since we have taken unit quantity of the substance G

$$[G] + [GM^+] = 1/(V + a)$$

or

$$[G] = 1/(V + a) - z \qquad (5)$$

where a is the initial volume of the colloid.

From (1) and (5)

$$(1/(V + a) - z)y = Kz \qquad (6)$$

and from (2) and (3)

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$$z = e + 2\sqrt{ey}$$

or

$$z = CV + 2\sqrt{CVy}. \tag{7}$$

From (6)

$$(V + a)(K + y)z = y$$

and substituting the value for z in (7)

$$(V + a)(K + y)(CV + 2\sqrt{CVy}) - y = 0 \tag{8}$$

where the only variables are V and y.

Since volumes are usually plotted as functions of x, it might seem preferable to substitute for y its equivalent function of V and x, for

$$2y = 2x + CV - \sqrt{4CVx + C^2V^2}.$$

But by so doing the equation becomes unnecessarily involved, since the Curve $V = f(x)$ can be plotted indirectly by giving successive values to y, solving for V, and then determining x from

$$x = y + \sqrt{CVy}.$$

It is evident that where any 2 variables are known all others can be calculated.

If the molecules or atoms of the colloid are not themselves permeable to all the ions considered, we believe that the quantity a should not be taken as the whole of the initial volume of the jelly, but only as the free space within the jelly through which the ions may pass. For our hypothetical substance, then, we shall consider the limiting case where the value of a is zero. Equation 8 thus reduces to

$$V(K + y)(CV + 2\sqrt{CVy}) - y = 0. \tag{9}$$

TABLE I.—SHOWING INTERRELATION OF VARIABLES AT EQUILIBRIUM.

$V(0.001 + y)(0.0001V + 0.02\sqrt{Vy}) - y = 0.$

y.	V.	z.	e.	s.	$y + s$.	Vs.
0.0005	44.7	0.00199	0.00447	0.0074	0.0079	0.333
0.0008	49.7	0.00279	0.00497	0.0090	0.0098	0.445
0.0009	50.7	0.00304	0.00507	0.0093	0.0102	0.474
0.0010	51.6	0.00327	0.00516	0.0097	0.0107	0.501
0.0020	55.0	0.00530	0.00550	0.0120	0.0140	0.662
0.0024	55.170	0.00604	0.00552	0.0128	0.0152	0.706
0.0025	55.176	0.00621	0.00552	0.0129	0.0154	0.712
0.0026	55.168	0.00638	0.00552	0.0131	0.0157	0.723
0.003	55.0	0.00706	0.00550	0.0136	0.0166	0.750
0.004	54.3	0.00866	0.00543	0.0147	0.0187	0.801
0.005	53.3	0.01016	0.00533	0.0157	0.0207	0.834
0.010	48.5	0.01696	0.00485	0.0188	0.0288	0.911
0.050	33.6	0.06296	0.00336	0.0293	0.0793	0.984
0.100	27.5	0.11658	0.00275	0.0360	0.1360	0.990
1.000	13.4	1.03661	0.00134	0.0745	1.0745	0.999

Table I and Fig. 1 were prepared by taking the arbitrary values $C = 10^{-4}$ and $K = 10^{-3}$, substituting successive values for y, and solving by a

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method of approximation for one real root, the corresponding root being taken in each case; from V and y all other variables were obtained by

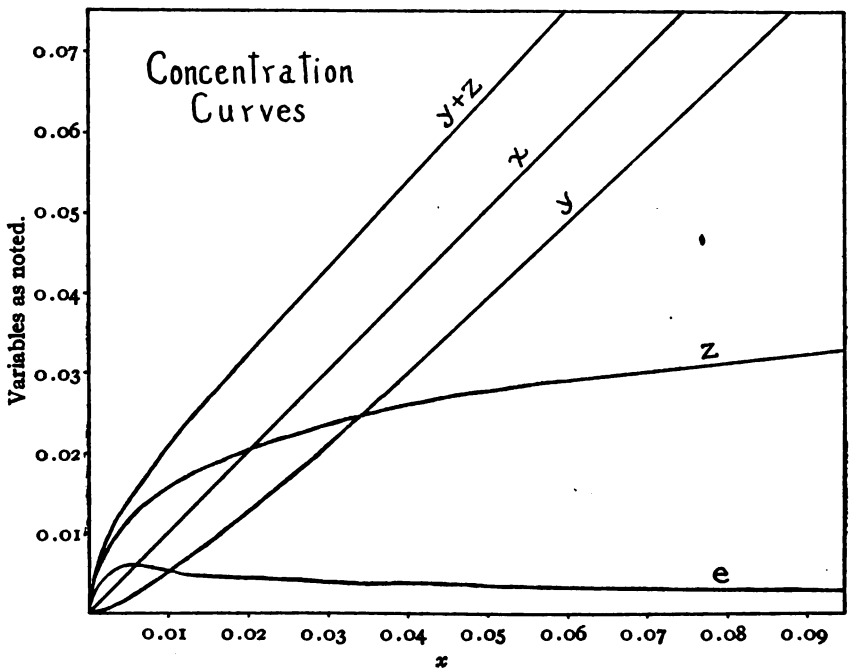

Fig. 1.

substituting in equations already given. A similar method was used in plotting the family of curves in Fig. 2, which is self-explanatory.

All of these curves are of the same nature as many corresponding ones obtained by experiment upon various colloid jellies and electrolytes.[1]

The Case of Several Binary Electrolytes and a Colloid Jelly which Combines with Some, but not All, Ions of One Sign.

From the derivation of Equation 2 it is evident that the product of concentrations of the oppositely-charged ions of any electrolyte must be the same in both phases, making it possible to broaden the system of notation so that in the external solution

[1] Since writing this paper, one of us has prepared a reply on the theory of tanning, which has been sent to the *Journal of the American Leather Chemists' Association* for publication. In this paper it is mentioned that Procter and Wilson obtained the value $K = 1.5 \times 10^{-4}$ for gelatin and hydrion by adding successive portions of HCl to a gelatin solution and determining the hydrion concentration after each addition by means of the hydrogen electrode. They obtained the value $C = 3 \times 10^{-4}$ from experimental values for e with Coignet's gelatin at 18°. Using these 2 constants in Equation 9 and solving for all variables, curves were obtained which are in rigid quantitative agreement with all of the experimental curves for gelatin and HCl solutions at 18°.

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x = sum of concentrations of all positive or negative ions and in the jelly phase.

y = sum of concentrations of all diffusible ions of the same sign as that of the colloid ions.

z = sum of concentrations of colloid ions.

Equations 2 and 3 can now be re-derived and their simultaneous solution gives

$$e = -2x + \sqrt{4x^2 + z^2}$$

or

$$CV = -2x + \sqrt{4x^2 + z^2}. \qquad (7)$$

Whenever an electrolyte is added to the system, if it combines with G, then the value of z is increased; otherwise x is increased. If the value of x is raised while z remains constant, the volume must fall. Likewise the volume will increase if z, but not x, is augmented. By applying the calculus, it is found that to effect an increase in volume the rate of in-

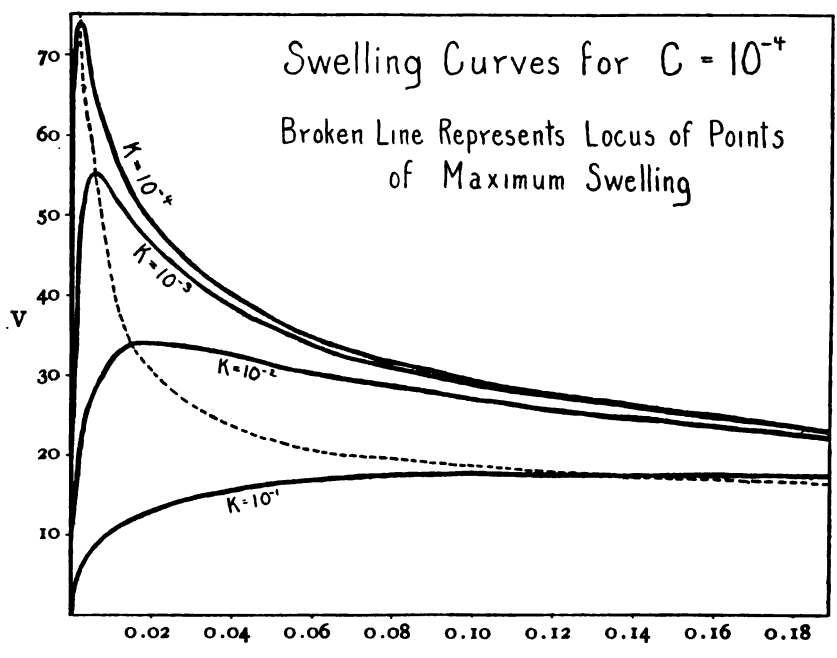

Fig. 2.

crease of z must be made greater than $2e/z$ times that of x. The addition of any electrolyte which does not combine with G must cause contraction of the swollen jelly to the extent to which it increases the ionic concentration, while adding one which does combine with the colloid will produce either swelling or contraction depending upon the value of dz/dx. This

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statement would have to be modified, however, if any one of the colloid compounds were not wholly ionized. Any combination between the colloid ion and a diffusible ion of opposite sign would decrease the value of z and cause contraction of the jelly.

The Presence of Polyvalent Ions.

Suppose that G were to combine with the positive but not the negative ion of the electrolyte MaN. Using the method by which Equation 2 was derived,

$$x^{a+1} = y^a(y + z)$$

from which it is mathematically apparent that

$$(a + 1)y + z > (a + 1)x$$

or that

$$(a + 1)y + z = (a + 1)x + e.$$

Although the relations are now more complex, it is still clear that the addition of MaN to G will produce swelling and that when G becomes nearly saturated, contraction of the jelly is the necessary concomitant of any further addition of electrolyte. As a matter of fact, however, we should not expect this colloid salt with a polyvalent negative ion to be highly ionized, and if *it* were not, the value of z would be correspondingly smaller, there would be less swelling, and our equations for the volume would be worthless unless we took into consideration the actual degree of ionization of the colloid salt.

A general mathematical treatment of the whole subject is desired and it is to be hoped that it will soon be undertaken, but in the present paper it has been deemed sufficient to derive volume equations only for binary electrolytes, as the purpose in view is only to give an outline of the general mechanism of the swelling of colloid jellies rather than to explain the peculiarities in the swelling curves of polybasic acids upon certain proteins.

General Nature of the Equations.

Equations 2, 3 and 7 were not derived upon the assumption that any chemical combination had taken place, but that $[M^+]$ and $[N^-]$ were unequal in one phase and equal in the other and they are therefore applicable to any such 2-phased systems. The particular curve for z in Fig. 1, on the other hand, does assume actual combination because it is taken as proportional to the product of the concentrations of the combining substances. The volume curves in Fig. 2 also assume chemical combination.

Relation of Physical Constants to the Point of Maximum Swelling.

The broken line in Fig. 2 represents the locus of all points of maximum swelling for one millimole of G whose value for $C = 10^{-4}$. By the variation of C, an area is generated which is a function of C, x, and V, and repre-

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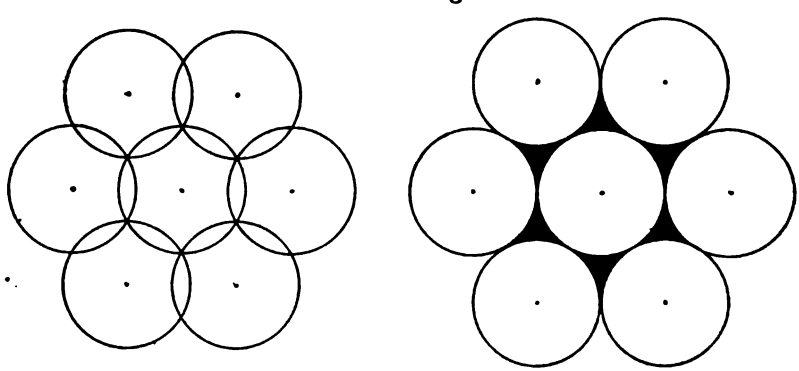
sents the locus of all points of maximum swelling for one millimole of every colloid jelly with the properties of G, when immersed in solutions of MN of varying concentration. This standard curve might be used to test the validity of the assumptions. Suppose the bulk modulus of a certain protein had been determined by elasticity experiments to correspond to $C = C'$, and that when immersed in varying strengths of a binary electrolyte its maximum volume per milligram was found to be V' cubic centimeters at $x = x'$. Erect a perpendicular to the plane Cx at the point C', x', o. It will intersect the standard curve at V, the maximum volume of one millimole. The equivalent weight of the protein is V/V', which should equal the numerical value of the number of grams of the protein which combine with a maximum of one mole of MN.

Continuity of the Phases.

In the foregoing discussion of 2-phased systems, each phase has been assumed to be continuous. This is not the case when the system becomes a sol, and it is therefore interesting to examine the transition from one state to the other. In the colloid ions GM^+, the M^+ ions will be in direct combination only with certain isolated atoms (say A) and consequently the negative ions cannot diffuse to more than a certain average distance from their corresponding positive colloid ions unless replaced by their equivalent value of ions of the same sign. Consider a cross-section of



$n = r\sqrt{3}$. $n = 2r$.

Fig. 3.

the jelly and assume for the sake of simplicity that each positively-charged A atom is immediately surrounded by and equidistant from six others, which distance we may call n. Denote the average distance which a negative ion may move from its corresponding A atom by r, which might be termed its radius of action. A glance at Fig. 3 will show that so long as $n < r\sqrt{3}$, the jelly-phase as well as the external solution will be continuous. It will be seen, however, that between $n = r\sqrt{3}$ and $n = 2r$, the jelly-phase will still be continuous, but the solution phase will be dis-

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continuous. The black regions in the figure show isolated sections of external solution distributed throughout the jelly. It is suggested that certain microscopic pores found in hardened jellies may have had their origin in these isolated portions of solution. When $n > 2r$, the solution phase again becomes continuous, the jelly-phase discontinuous and the system a sol.

The Empirical Adsorption Formula.

The voluminous literature which has appeared dealing with "adsorption isotherms" lends an added significance to the curve for z in Fig. 1, which by its derivation represents the concentration of electrolyte chemically combined with the colloid, *i. e.*, $[GM^+]$. Not being aware of this, one might be tempted to try to fit it to the empirical adsorption formula $z = ax^{1/n}$, and assuming slight discrepancies to be due "to experimental error," to announce that the phenomenon had been proved to be purely physical. By substituting 2 sets of values for z and x in this equation and solving for the constants, we get $a = 0.073$ and $1/n = 0.335$. In Table II there are given actual values of z taken from the curve, together

TABLE II.—COMPARISON OF VALUES CALCULATED FROM EMPIRICAL ADSORPTION FORMULA AND THOSE CALCULATED FROM EQUATIONS GIVEN IN THIS PAPER.

x.	z.	$0.073x^{0.335}$.	$V(y+z)$.	$14x^{0.56}$.
0.003	0.009	0.010	0.52	0.54
0.006	0.013	0.013	0.84	0.80
0.010	0.016	0.016	1.10	1.06
0.017	0.019	0.019	1.40	1.43
0.063	0.029	0.029	2.66	2.98
0.117	0.036	0.036	3.74	4.21
1.000	0.074	0.073	14.4	14.0
10.000	0.159	0.158	64.0	50.8
100.000	0.341	0.341	191.0	185.0

with values calculated from the adsorption equation upon the assumption that

$$z = 0.073\,x^{0.335}.$$

The results are in fully as close agreement as is general when observed results are compared with calculations from the empirical formula.

Examination of an earlier paper[1] by one of us will show that the above relations are equally applicable to suspensoids or any other colloids, even when these are impermeable to water. Suppose that a suspensoid S is impermeable to water, but that its surface molecules will combine chemically (say by reason of their residual valencies) with the positive ion of a binary electrolyte forming the completely ionized compound SMN only at the surface of S. The surface film of solution surrounding the particles will have a greater concentration of N^- than of M^+ and consequently

[1] THIS JOURNAL, 38, 1982 (1916).

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when equilibrium has been established, the relations existing between the concentrations of the ions of the surface film and those of the bulk of solution will be expressible by Equations 2 and 3 given above, but where in the bulk of solution

$$x = [M^+] = [N^-],$$

and in the surface film

$$y = [M^+], \text{ and } y + z = [N^-]$$

and e = the necessary excess concentration of diffusible ions of the surface film over that of the bulk of solution. One millimole of S is defined as that weight of S whose surface molecules can combine with a maximum of one millimole of MN, and this weight will naturally vary with the degree of dispersion. V is defined as the volume in cubic centimeters of the surface film surrounding one millimole of S. As e becomes greater, the resulting increase of outward diffusion pressure will cause an increase in the size of the particles with a corresponding increase in V. It is now clear that the relations derived for colloid jellies differ from those of other dispersoids only in degree.

Since, according to the empirical formula, z becomes continually greater as x increases without limit, this formula is quite incompatible with that for chemical combination where only one phase and no alteration in volume are concerned, for in

$$z = ay/(K + y),$$

as y increases without limit, z approaches the constant a. If V be assumed constant and z be plotted against x, the curve will be rounded off, since x increases at a greater rate than y, and therefore within certain fixed limits z may more nearly approximate values obtained by use of the empirical formula, but the formulas are still incompatible since z has a finite limit. But according to the reasoning given for colloid jellies, the limit of V, as x increases without limit, is zero and consequently z has no finite limiting value and the above-mentioned incompatibility between the 2 formulas vanishes.

Since the empirical formula is concerned rather with the total quantity of electrolyte adsorbed, whether chemically combined with the colloid or merely in solution in the surface layer, the curves from this formula should be compared with those for the quantity $V(y + z)$. In Table II are given values for this quantity taken from Table I along with the corresponding values for $14x^{0.56}$, from which it will be seen that the two values do approximate each other over wide ranges of concentration. The authors believe that further development of the above reasoning will finally result in the derivation of a formula for adsorption which will be more satisfactory than the one now so widely employed.

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Summary.

The radical difference between the theory of the molecular mechanism of protein swelling presented by Tolman and Stearn and that evolved by Procter and Wilson is pointed out.

It is shown that if a colloid jelly combines chemically with a given electrolyte forming a highly ionizable colloid salt, the jelly must swell to a maximum and then contract indefinitely as the concentration of ionized electrolyte in the solution is increased.

It is shown further that the addition to the system of any electrolyte which does not combine with the colloid will produce contraction of the swollen jelly to an extent depending upon the resulting increase in ionic concentration.

A suggestion is given as to the origin of microscopic pores observed in certain hardened jellies.

Upon the assumption that a colloid combines chemically with ions of one sign of a dissolved electrolyte, both the concentration of chemically combined electrolyte and the total quantity of electrolyte either combined with or present in the solution in contact with the colloid are represented as functions of the concentration of electrolyte in the solution. The curves for these functions are approximately the same as those obtained by use of the empirical adsorption formula. It is believed that further development of the reasoning given in this paper will result in a more satisfactory formula for adsorption than the one now so generally used.

The authors wish to express their thanks to the Editors of THIS JOURNAL for their helpful criticism of the manuscript before publication.

THE USE OF HYDROFLUORIC ACID IN ANALYSIS.

BY N. HOWELL FURMAN.

Received February 15, 1918.

Introduction.

In recent years a number of new analytical procedures have been developed which are based upon the behavior of certain fluorides in neutral and acid solution. The main chemical facts of which use is made in these procedures are:

First, by choosing the proper solvent true solutions of the metals of the copper-tin group, or of the metals chromium, tungsten, and molybdenum, may be obtained. Indeed, nearly all of the metals, especially those most frequently found in alloys, are readily soluble in a mixture of nitric and hydrofluoric acids.

Second, having obtained such solutions, a number of separations which are difficult, or impracticable by any other known method, may be effected quickly and completely by the use of reagents commonly employed in analysis.

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The qualitative behavior of certain fluoride solutions has been investigated by A. A. Noyes, and the results of his experiments are to be found in "A System of Qualitative Analysis Including Nearly All of the Metallic Elements."[1] In this work some separations were mentioned as affording promise from a quantitative standpoint, although no effort was made to establish the fact that such separations were quantitative, and the hope was expressed that others would find opportunity to develop this field.

A study of the quantitative separations possible in such solutions was undertaken by L. W. McCay,[2] and the results thus far obtained show clearly that several types of alloys whose analysis was previously a difficult and tedious task can now be analyzed rapidly[3] and accurately by the aid of these new methods.

A list of the separations which can be effected in acid fluoride solution is given in Table I. An examination of this list will give some idea of the wide variety of alloys and ores to which the methods of separation can be applied. In this table a plus sign indicates that the element can

TABLE I.—ANALYTICAL SEPARATIONS POSSIBLE IN ACID FLUORIDE SOLUTION.

(*a*) Electro-Analytical Separations.

Element remaining in solution.	Element precipitated.			
	Copper.	Lead.	Silver.	Mercury.
Stannic tin	+	+	*V*	+
Antimony (ic)	+	+	*V*	+
Arsenic (-ic)	*V*			
Tungsten	+	+	*V*	+
Molybdenum	+	+	*V*	*V*
Chromium	+	+	*V*	+
Vanadium	+			

(*b*) Using Hydrogen Sulfide as Precipitating Agent.

Element remaining in solution.	Element precipitated.					
	Copper.	Lead.	Silver.	Mercury.	Antimony(-ous).	Arsenic(-ous).
Stannic tin	+	+	*N*	*N*	+	+
Tungsten	*N*	*N*	*N*	*N*		

All of the separations indicated above are known to be quantitative except those marked *N*, which are mentioned in the work of Noyes to which reference has been given, and which are in all probability quantitative.

[1] *Tech. Quart.*, 16, 93(1903); 17, 214 (1904).

[2] L. W. McCay, "The Separation of Tin and Antimony," THIS JOURNAL, 31, 373 (1909); "The Analysis of the Tin-Antimony Alloys," *Ibid.*, 32, 1241 (1910); "The Use of Hydrofluoric Acid in the Separation of Copper and Lead from Tin and Antimony by Means of the Electric Current," *Ibid.*, 36, 2375 (1914); L. W. McCay and N. Howell Furman, "The Use of Hydrofluoric Acid in the Separation of Some Heavy Metals from Tin, Antimony, Tungsten, and Molybdenum by Means of the Electric Current," *Ibid.*, 38, 640 (1916).

[3] Preliminary experiments indicate that Babbitts and other tin-antimony alloys may be analyzed in less than 8 hours' working time by these methods.

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be precipitated quantitatively from a solution containing all of the elements listed; *V* indicates a separation in which the voltage cannot exceed a definite maximum value.

An illustration will perhaps make the use of the above table more clear. The table shows that it is possible, for example, to separate quantitatively, copper, or lead, copper, silver, and mercury simultaneously from *one* or *all* of the elements—tin(-ic), antimony(-ic), tungsten, molybdenum, and chromium—by means of the electric current in hydrofluoric acid solution. If hydrogen sulfide be used as the precipitating agent, copper, lead, silver, mercury, antimony (-ous), and arsenic (-ous), can be separated individually, or collectively, from tin(-ic), and undoubtedly from tungsten as well.

The references which are cited in footnote 1 should be consulted for the precise conditions which are necessary in effecting a given separation.

Work is being continued by the writer and others upon several of the separations mentioned, and incidental observations upon the behavior of some metals not mentioned in the list are being made, with the idea of making the hydrofluoric acid method as comprehensive as possible.

The Separation of Copper and Vanadium.—The experimental data proving that copper can be separated quantitatively from vanadium by means of the electric current in acid fluoride solution are given in Table II. Weighed amounts of sodium vanadate were dissolved in water, 2.5 cc. of nitric acid, sp. gr. 1.4, and suitable amounts of hydrofluoric acid were added, and a definite amount of a standard copper nitrate solution was run in. The total volume of the solution was 100 to 110 cc. The current was maintained at 0.2 amp. $N.\ D._{100}$ and 2.5 to 4.5 volts for 8 to 10 hours, or overnight.

TABLE II.—THE SEPARATION OF COPPER AND VANADIUM.

Vanadium. G.	Hydrofluoric acid, 48% cc.	Copper taken. G.	Platinum found. Mg.	Copper found.[1] G.
0.1694	0.0	0.2506	0.1	0.2500
0.1479	5.0	0.2506	0.4	0.2508
0.1645	0.0	0.2506	0.2	0.2504
0.1773	5.0	0.2506	1.8	0.2505
0.1938	5.0	0.5012	1.3	0.5017
0.1941	2.5	0.5012	0.4	0.5008

It is evident that vanadium behaves just as do tin, tungsten, etc., in

[1] These copper values are corrected for the amounts of platinum indicated in the fourth column of the table. In the first 3 and the last determinations an anode of platinum-iridium was used. In such cases the amount of platinum deposited with the copper is almost invariably less than 0.5 mg. When an anode of pure platinum is used the amount deposited with the copper is much greater as shown in the fourth and fifth determinations in Table II. See McCay, THIS JOURNAL, 36, 2376 (1914).

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similar solutions. A few preliminary observations upon uranium and titanium seem to indicate that they too may be separated from copper, and without doubt from other elements by the same method.

A preliminary note has appeared indicating that cobalt and nickel[1] can be separated in ammoniacal fluoride solution, and there may be other separations possible in neutral or alkaline fluoride solutions. Little work has been reported in this field.

The Behavior of Stannic Tin in Acid Fluoride Solution.

Several elements when in the higher state of oxidation, in a solution containing free hydrofluoric acid, show a chemical deportment utterly different from that which they exhibit in a similar acid solution, which, however, contains no hydrofluoric acid. This behavior is the basis of the separations given in Table I. It may be illustrated in the most striking manner by the facts relating to stannic tin.

STANNIC TIN IN ACID SOLUTION.

	With a moderate amount of free hydrofluoric acid.	Without hydrofluoric acid.
1 Action on dilution....	No hydrolysis on great dilution, or after long standing.	Hydrolysis on moderate dilution, or on standing.
2 Electric current.....	No reduction with electromotive forces as great as 9 volts, and current densities as high as 5 amperes $N.D._{100}$ on a mercury cathode.	Reduction to the metal.
3 Action on boiling with zinc or aluminium....	No reduction to the stannous condition or metallic state after prolonged boiling.	Reduction to the stannous condition and metal.
4 Effect of hydrogen sulfide.....	Not a trace of precipitation on long-continued passage of the gas even when the solution is boiled.	Complete precipitation as stannic sulfide.
5 Effect of neutralization.....	The tin in such solutions cannot be estimated by neutralizing, and "salting out" the stannic hydroxide, for considerable amounts of tin remain in soluble form.	A satisfactory determination of the tin may be made by neutralizing, and "salting out" the stannic hydroxide.

It is evident that acid solutions of stannic fluoride containing free hydrofluoric acid in sufficient amount give none of the characteristic reactions of the stannic ion. Similar facts about the behavior of antimony, tungsten, and molybdenum, in their highest states of oxidation, are given in a previous paper.[2]

[1] E. F. Smith and H. S. Lukens, *Trans. Am. Electrochem. Soc.*, 27, 30 (1915).

[2] McCay and Furman, *Loc. cit.*

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It is likewise obvious that this behavior of stannic tin, which is of value in its separation from other metals, makes its subsequent estimation a matter of difficulty. The estimation of the tin is the largest time-consuming factor in the analysis of tin-antimony alloys by the hydrofluoric acid method,[1] of which a brief schematic representation is given below.

The Analysis of Tin-Antimony Alloys by the Hydrofluoric Acid Method.—The alloy is dissolved in hot conc. sulfuric acid and the cold solution poured into water containing hydrofluoric acid.[2]

PRECIPITATE: Lead sulfate.

FILTRATE: Copper, antimony, in the trivalent condition, tin in the stannic form, and a trace of lead.

When the filtrate is treated with hydrogen sulfide the copper, lead and antimony are completely precipitated as sulfides, which, after filtration, are digested with colorless potassium sulfide solution.

PRECIPITATE: Consisting of copper and lead sulfides is ignited; the residue is dissolved in nitric acid and the copper and lead determined electrolytically.

FILTRATE: Is heated with conc. sulfuric acid until the antimony sulfide is dissolved. The metal is then estimated volumetrically with standard potassium permanganate or bromate solution.

The filtrate containing the tin is evaporated in a platinum dish until the hydrogen fluoride is removed and the sulfuric acid has commenced to fume copiously. The tin may then be determined as stannic oxide, after the sulfuric acid solution has been poured into a large volume of water, the stannic hydroxide salted out and collected by filtration.

If the tin filtrate could be made to exhibit the properties of stannic ions, and if the use of platinum could be avoided, the value of the method would be greatly enhanced. In a recent article by O. L. Barneby[3] it is stated that in determining ferrous iron with potassium permanganate in solutions of rock powders in hydrofluoric and sulfuric acids, satisfactory results are obtained by adding boric acid to the solutions prior to titration. Ordinarily the manganous fluoride generated in such solutions is oxidized by the permanganate used in the titration, and the red-brown tint of the undissociated manganic fluoride formed obscures the end-point. The addition of a moderate excess of boric acid removes the fluorine from the sphere of action, possibly by the formation of the complex acid, HBF_4, thus making it possible to obtain a satisfactory end-point in the titration. After the addition of the boric acid the ferrous iron solutions are as stable in air as are sulfuric acid solutions of ferrous sulfate. Titanic, molybdic, and silicic acids act in a manner similar to boric acid.

[1] THIS JOURNAL, 32, 1241 (1910).

[2] The water and hydrofluoric acid are contained in a ceresin beaker. A funnel which has been paraffined is used in the filtration.

[3] *Ibid.*, 37, 1481 (1915).

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These facts at once suggested the possibility of causing a hydrofluoric acid solution of stannic tin to behave like an ordinary acid solution of the metal, by the addition of a moderate amount of boric acid. A thorough test of this possibility was made with complete success, not only from a qualitative standpoint, but from a quantitative one as well, as the following experiments show.

The Precipitation of Tin as Sulfide in the Presence of Hydrofluoric and Boric Acids.—Weighed portions of metallic tin of tested purity were dissolved in 5 cc. hot conc. sulfuric acid, and the resulting solutions poured into a platinum dish containing water and 2 cc. of 48% hydrofluoric acid. A slight excess of solid boric acid was added, and, after dilution to 200–250 cc., the solution was warmed and a rapid stream of hydrogen sulfide gas run in for at least half an hour. After standing until the precipitate had settled the sulfide was filtered off, washed thoroughly with 0.5% ammonium chloride solution and then with alcohol. The sulfide was transformed into the oxide by roasting, observing the usual analytical precautions. The results are given in Table III.

TABLE III.—DETERMINATION OF TIN AS SULFIDE IN SOLUTIONS CONTAINING HYDROFLUORIC AND BORIC ACIDS.

Tin taken. G.	Boric acid. G.	Residue from filtrate. Mg.	Tin found. G.
0.1014	5.0	1.0	0.1013
0.1000	5.0	0.3	0.0990
0.2013	3.0	0.2	0.2019
0.2029	3.0	0.3	0.2020
0.2009	4.0	0.2	0.2003

In the third column are given the weights of material recovered from the filtrate after filtering off the stannic sulfide precipitates. These filtrates were in each case evaporated in platinum until the hydrogen fluoride was completely removed. Sufficient water was then added to dissolve the boric acid which had separated out, and hydrogen sulfide was passed through the solution for 15 to 20 minutes. A slight yellow color appeared, and after standing 12 to 18 hours, a small amount of a light brown precipitate had settled out. This precipitate was collected, ignited, and the residue weighed. In only one case was the residue as great as one mg.; in this case the bulk of the residue was found later to be platinum, which had been dissolved from the dish by the action of the sulfuric acid.[1] The other residues also consisted mainly of platinum.

Electrolytic Precipitation of Tin from Solutions Containing Hydrofluoric and Boric Acids.—Solutions of tin were prepared exactly as described above. To each solution, after the addition of boric acid, 5 g. of ammonium oxalate and 5 g. of oxalic acid were added, the final volume

[1] See L. W. McCay, "The Action of Boiling Sulfuric Acid on Platinum," *Reports 8th Internat. Cong. Applied Chem.*, 1, 351 (1912).

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of the solution being brought to 300 cc. The deposition of the tin was effected under the conditions of current recommended by Classen.[1] The cathodes used were coated with copper to prevent the alloying of the platinum with tin, which otherwise takes place. The tin was deposited completely from this solution, but the time required was excessive (48 hours). The results are given in Table IV.

TABLE IV.—ELECTROLYTIC DEPOSITION OF TIN FROM SOLUTIONS CONTAINING HYDROFLUORIC AND BORIC ACIDS.

Tin taken. G.	Boric acid. G.	Hydrofluoric acid, 48% cc.	Platinum found. Mg.	Tin found.[2] G.
0.1076	2.0	1.0	0.5	0.1065
0.1020	3.0	2.0	1.5	0.1022
0.2003	3.0	2.0	1.6	0.2009
0.2074	4.0	2.0	1.1	0.2071
0.2072	3.0	1.0	0.7	0.2062

The solutions from which the tin had been deposited were tested for the presence of tin in the following manner: After being made ammoniacal, the solution was saturated with hydrogen sulfide gas, then made faintly acid with acetic acid; the precipitate formed was filtered off, ignited, and weighed. In no case was the weight of the residue greater than 0.3 mg., nor could tin be detected therein.

Reduction of Stannic Tin by Metals in Solutions Containing Hydrofluoric and Boric Acids.—Acid fluoride solutions of stannic tin to which an excess of boric acid had been added were found to be reduced by metallic zinc or aluminium, the tin of course being reduced to the metallic state.

The Hydrolysis of Stannic Tin Salts in the Presence of Hydrofluoric and Boric Acids.—When a solution of stannic tin, prepared as above, is rendered ammoniacal, then very slightly acid with sulfuric acid, it undergoes partial hydrolysis on standing or on being diluted to a sufficient degree. The precipitated stannic hydroxide settles well and may readily be filtered off. The hydrolysis is never complete, however, for if hydrogen sulfide be run into the filtrate, a yellow coloration appears almost immediately, and a considerable amount of stannic sulfide is precipitated.

The Use of Silica Instead of Boric Acid.—Since silicon has a very great affinity for fluorine, it seemed reasonable to suppose that its presence would cause tin to behave as if fluorine were absent, in much the same manner as boric acid does. Experiments of a purely qualitative nature proved that this was the case. If, for example, an excess of sodium silicate is added to an acid solution of stannic fluoride, the tin may be completely precipitated by hydrogen sulfide.

[1] "Quant. Analysis by Electrolysis," 1915, p. 135.

[2] The tin values are corrected for the weights of platinum given in the fourth column of the table.

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Experiments showed that silica itself is not very effective in counteracting the effect of the fluorine, owing to the difficulty with which *dilute* solutions of hydrofluoric acid attack it. It was found that silica prepared by purifying a sample of kieselguhr with hydrochloric acid and subsequent water extractions, when placed in large excess in one of the tin solutions, did not combine with the fluorine to an extent sufficient to permit even a trace of tin to be precipitated by hydrogen sulfide, although the solution was boiled for half an hour and allowed to stand overnight in an atmosphere of hydrogen sulfide, after saturation with the gas.

Silica prepared by the dehydration of silicic acid precipitated from water glass was found to be fairly reactive, and with its use a complete precipitation of the tin as sulfide could be made after sufficient boiling.

The Action of Solutions Containing Hydrofluoric and Boric Acids upon Glass.—The above experiments suggested the possibility that fluoride solutions to which boric acid had been added in excess would have little action on glass vessels. A beaker of good American glass, weighing at the outset 97.16 g., was subjected to the action of a solution containing 2 cc. of 48% hydrofluoric acid, 0.5 cc. of 5 *N* sulfuric acid, and 4 g. of boric acid per 300 cc. The average loss in weight was found to be 0.00049 g. per 24 hours, per 100 cm^2. of exposed surface, at room temperature. Omitting the boric acid, the average loss was 0.088 g. per 24 hours per 100 cm^2. of exposed surface.

When one of the solutions containing boric acid was boiled for half an hour, the loss which the beaker suffered was about equal to that occasioned by 2 days' action of the solution at room temperature.

Solutions which contained no hydrofluoric acid attacked the beaker to the extent of 0.5 mg. at most, under the conditions which prevailed in the above experiments.

It is apparent that boric acid exerts a very marked protective action. These results show that glass vessels may be used in qualitative and quantitative work with such solutions, since the material removed from the glass is moderate in amount, and remains in a soluble form. As a matter of fact, the last 2 electrolytic determinations given in Table IV were made in glass beakers.

The scheme for the analysis of tin-antimony alloys, which is outlined on page 899, is modified to avoid the use of platinum vessels as follows:

The filtrate containing the tin is collected in a glass beaker in which a solution containing the requisite amount of boric acid has been placed. The acidity of the solution is adjusted by the addition of ammonium hydroxide until 0.5 cc. or less of 0.5 *N* acid remains. The tin is then precipitated by hydrogen sulfide and estimated in the form of tin dioxide.

The Qualitative Analysis of the Tin Group.—The facts above presented,

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together with others previously known about the behavior of certain fluorides in solution, lend themselves readily to a method for the qualitative examination of the tin group of elements, which is outlined below.

Dissolve the tin group precipitate in 10 cc. of hot conc. sulfuric acid.[1] Pour the resulting solution into water containing hydrofluoric acid and run in hydrogen sulfide until the precipitation is complete.

PRECIPITATE: Arsenious and antimonious sulfides.

Treat with hydrochloric acid and potassium chlorate.

One portion of the resulting solution is diluted considerably. A red precipitate formed when hydrogen sulfide is introduced indicates antimony. The presence of antimony is confirmed by a suitable test.

The other portion of the solution is divided into two equal parts.

To the first is added two or three times its volume of conc. hydrochloric acid. A yellow precipitate formed when hydrogen sulfide is run in indicates arsenic.

The second part of the solution is made ammoniacal, filtered, and the formation of a white crystalline precipitate on the addition of magnesia mixture to the filtrate indicates arsenic.

FILTRATE: Stannic fluoride in solution.

Add an excess of solid boric acid and heat until solution is complete. Precipitate the tin with hydrogen sulfide, dissolve the precipitate in conc. hydrochloric acid, and make the usual confirmatory test.

As a test of this procedure, a number of unknowns were examined, which Mr. L. B. Dobie, Assistant in Quantitative Analysis, kindly prepared. These solutions were made from stock solutions of copper, arsenic, antimony, and tin, each solution containing 0.50 g. of metal per 50 cc., so that the amount of metal present was known quantitatively in each case. The procedure used was as follows:

The copper-tin group precipitate was treated with colorless potassium sulfide[2] in a porcelain dish at water bath temperature for 10 to 15 minutes, and the solution of sulfo-salts formed filtered directly into a tall narrow beaker, or Erlenmeyer flask of 200 to 300 cc. capacity, all unnecessary dilution being avoided. From 5 to 15 cc. of

[1] A small piece of sulfur is added so that the sulfur dioxide formed may reduce all arsenic and antimony to the lower state of oxidation.

[2] Colorless, freshly-made potassium sulfide is usually preferable for this separation, in alloy analysis. A separation of the copper and tin groups described by M. Cannon Sneed, THIS JOURNAL, 40, 187 (1918), involves the use of colorless sodium sulfide. The method of analysis of the tin group described above could be applied to the filtrate obtained in Sneed's method, after the removal of the mercury as carbonate. The use of yellow or colorless ammonium sulfide in the separation of the copper and tin groups does not alter the subsequent procedure for the analysis of the tin group by the hydrofluoric acid method.

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conc. sulfuric acid were added cautiously, a little at a time, after which heat was applied until the sulfides were completely dissolved.[1] By this treatment any antimony and arsenic in the higher states of oxidation were completely reduced to the lower state, while the tin remained entirely in the stannic condition.[2] When cool the solution was diluted somewhat and after cooling poured into 100 cc. of water containing 1 to 3 cc. of 48% hydrofluoric acid.[3] After a thorough mixing, a rapid stream of hydrogen sulfide gas was introduced until the precipitation of the arsenic and antimony was completed.

A portion of the well-washed precipitate was treated as follows: Solution and complete oxidation of both antimony and arsenic were effected by treatment with 10 to 20 cc. of conc. hydrochloric acid with the addition of small portions of potassium chlorate; the solution was boiled down to half of its volume, made up to the original volume with conc. hydrochloric acid, and again evaporated to half its volume.[4] Any free sulfur present was removed by filtration at this point.

One-half of this solution was diluted to a volume of about 600 cc., and a rapid stream of hydrogen sulfide run in for 5 minutes or so.[5] A yellow coloration, or reddish precipitate indicated antimony. After all excess of hydrogen sulfide had been expelled by a rapid current of filtered air, some of the well washed precipitate was subjected to one of the usual confirmatory tests for antimony.

Some of the remaining portion of the original solution was made ammoniacal, any precipitated antimony hydroxide removed by filtration and the filtrate tested with magnesia mixture. The formation of a white crystalline precipitate indicated, of course, the presence of arsenic.

As an alternative or confirmatory test for arsenic, some of the original solution was mixed with twice its volume of conc. hydrochloric acid, and a rapid stream of hydrogen sulfide gas then led in, the solution being well-cooled during the process. Under these conditions only arsenic in the form of the yellow pentasulfide[6] is precipitated.

A portion of the filtrate which may contain tin is poured into a glass beaker in which 2 to 4 g. of solid boric acid has been placed. Most of the free acid is neutralized by the addition of ammonium hydroxide, after which a rapid stream of hydrogen sul-

[1] This process can be completed in 40 to 60 minutes.

[2] Free sulfur is necessary for this reduction. This may be furnished by the decomposition of the sulfides, but it is safest to add a small piece of sulfur.

[3] The hydrofluoric acid solution is placed in a beaker made of paraffin or ceresin. An empty hydrofluoric acid bottle can be made into a beaker admirably suited for this sort of work. A paraffined funnel is used in the filtrations. Some sulfur separates when the solution of the sulfides is made, but this may be removed by filtration, most conveniently at this point.

[4] A. A. Noyes, "Qual. Analysis," 1915, p. 61; also Treadwell "Quant. Analysis," 1914, p. 241.

[5] This is an adaptation of Bunsen's quantitative method for the separation of antimony and arsenic (*Ann.*, 192, 305 (1878)). The arsenic remains in solution because of the formation of sulfoxyarsenic acids, especially monosulfoxyarsenic acid, H_3AsO_3S. For an account of the preparation, properties, and deportment with reagents, of these acids, see L. W. McCay, *Am. Chem. J.*, 10, 459 (1888); *Z. anorg. Chem.*, 29, 36 (1901); L. W. McCay and Wm. Foster, *Ibid.*, 41, 452 (1904); L. W. McCay, THIS JOURNAL, 24, 661 (1902); see also Wm. Foster, *Ibid.*, 38, 52 (1916).

[6] The procedure given follows the quantitative method devised by F. Neher, *Z. anal. Chem.*, 32, 45 (1893).

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fide gas is led in until precipitation is complete. A yellow precipitate indicates tin, whose presence is confirmed by the usual test with mercuric chloride solution.[1]

The procedure given for the separation and detection of arsenic and antimony is preferable to the treatment of the sulfides with conc. hydrochloric acid, in as much as arsenious sulfide is appreciably soluble in this acid, whereas the pentasulfide usually obtained in most procedures for the examination of the tin group, is practically insoluble in this acid. Good results were obtained by using hydrochloric acid of a concentration obtained by mixing 2 parts of the concentrated acid with one part of water. The sulfides were digested with this acid at water-bath temperature. Following the procedure outlined above there is no difficulty in detecting arsenic and tin in a solution containing 2 mg. of the former and 500 mg. of the latter per 200 cc., either in the presence of large or small quantities of antimony.

In Table V are summarized the results of the examination of the unknown solutions previously mentioned, together with the actual amounts of the metals present in each case; this latter information was supplied by Mr. Dobie after all the analyses had been completed.

TABLE V.—RESULTS OF EXAMINATION OF UNKNOWN SOLUTIONS.

	Copper.		Tin.		Antimony.		Arsenic.	
	Amount present. Mg.	Reported.	Amount present. Mg.	Reported.	Amount present. Mg.	Reported.	Amount present. Mg.	Reported.
1.	500	Abundant	0	Absent	0	Absent	0	Absent
2.	500	Abundant	100	Abundant	250	Abundant	500	Abundant
3.	500	Abundant	0	Absent	500	Large amount	2	Extremely small amount
4.	500	Abundant	500	Large amount	5	Very small amount	200	Large amount
5.	500	Abundant	2	Quite small amount	0	Doubtful	500	Large amount
6.	500	Abundant	200	Considerable amount	0	Absent	10	Small amount
7.	500	Abundant	2	Small amount	500	Abundant	0	Absent
8.	500	Abundant	5	Fair amount	5	Small amount	200	Abundant
9.	500	Abundant	10	Fairly small amount	200	Abundant	5	Small amount

Comments on Examination of Unknown Solutions.—In each case the original volume of the unknown solution was 200 cc. Not more than 50 cc. of each solution was taken for examination.

It will be noticed that in the fifth unknown the presence of antimony is reported as doubtful. No antimony was placed in this solution. Aside from this error, there is in every case at least qualitative agreement. The quantities of metals reported agree to a fair extent with the amounts actually present. The amount of tin reported in the ninth unknown was

[1] In the examination of some of the unknowns a positive indication of the presence of tin was obtained, both by the mercuric chloride test and the formation of a yellow precipitate, when the amount of tin actually present was later calculated to be less than 0.3 mg. in 30 cc. of the solution tested. This fact is an indication of the completeness with which the tin is precipitated, and the fluorine held in combination, through the agency of the boric acid.

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taken to be about the same as that in the eighth, while that in the seventh was thought to be slightly greater than that in the fifth, but there was no doubt in any of these cases as to the actual presence of tin.

In no case was any tin found with the arsenic, or antimony, nor could a trace of these elements be detected in the tin filtrates.

Summary.

A review of the established quantitative separations of metals in hydrofluoric acid solution, which have been described in various separate papers, was made in order to call attention to the possibilities of their use in the analysis of various types of ores and alloys. Some new quantitative separations have been described.

A further study of the effect of adding boric acid to hydrofluoric acid solutions of various substances has shown that the virtual removal of the fluorine from the field of action, which has been previously described by others, may be applied in making the analysis of the tin-antimony and other types of alloys more rapid and economical. This principle was also found useful in a modified scheme for the qualitative examination of the tin group of elements.

The effect obtained by adding boric acid to hydrofluoric acid solutions of various substances suggests further applications than those described, some of which are being investigated.

In conclusion, the writer wishes to express his thanks to Dr. L. W. McCay for the inspiration and guidance which made this work possible. He wishes also to acknowledge the valuable advice and assistance given to him by Dr. E. C. Franklin in the revision of this paper.

PRINCETON, N. J.

THE BEHAVIOR OF SOLUTIONS OF STANNIC FLUORIDE.

BY N. HOWELL FURMAN.

Received February 15, 1918.

Introduction.

In the preceding paper the analytical deportment of acid solutions of a variety of metals, with free hydrofluoric acid present, and the absence under these conditions of some or all of the characteristic reactions of the ions of the metals, tin, tungsten, molybdenum, antimony, chromium and vanadium, in their highest states of oxidation, has been described. The following investigation of some of the properties of stannic fluoride solutions was made in the hope that it would explain, or at least throw some light on, the reasons for the observed facts.

Stannic fluoride cannot be prepared by the evaporation of its aqueous solutions, for oxyfluorides, and eventually stannic oxide itself are formed;[1]

[1] Berzelius, *Traité de Chimie*, 4, 124 (1847).

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nor has the compound been prepared by heating any of its dry double salts.[1] Thus far the only successful method for its preparation is that of Ruff and Plato,[2] based on the reaction

$$SnCl_4 + 4HF = SnF_4 + 4HCl\uparrow$$

with the use of strictly anhydrous materials, platinum apparatus, and with the rigid exclusion of moisture.

The product obtained by these investigators, and subsequently by Wolter,[3] using the same apparatus, has the following properties:

It is a snow-white, crystalline solid, extremely hygroscopic, which sublimes at 705°, and has a density of 4.780 at 19°. It dissolves in water with a hissing sound, liberating heat, and yielding a clear solution which becomes turbid on standing, or on boiling, eventually undergoing complete hydrolysis. When such a solution is made acid with hydrochloric or sulfuric acid, the tin is precipitated very slowly, though completely, by hydrogen sulfide. In addition to the double salts described by Marignac,[4] it forms the following double compounds: SnF_4SnCl_4,[5] SnF_4NH_3, $SnF_4.2NH_3$.[6]

Dry hydrogen sulfide gas has little or no action on dry stannic fluoride, but with liquid hydrogen sulfide a violent double decomposition takes place according to the equation

$$SnF_4 + 2H_2S = SnS_4 + 4HF.$$

(This is a difference in chemical deportment from that of the chloride, for the latter substance forms an addition compound under similar conditions.)

Stannic fluoride is reduced with violence by metallic zinc or aluminium, but the formation of the intermediate bifluoride was not observed in Wolter's experiments.[6] The chlorides and oxychlorides of phosphorus enter into simple double decomposition reactions with stannic fluoride.

Experimental.

Preparation of Pure Hydrofluoric Acid.—The method of Ruff and Plato was used for the preparation of stannic fluoride. The apparatus will be readily understood from Fig. 1. Anhydrous hydrofluoric acid was prepared by heating dry potassium-hydogen fluoride in the platinum vessel *A*.[7] The hydrofluoric acid vapor passed into the copper condenser *B*, and was collected in the copper flask *C*, both of these portions of the

[1] O. Ruff, *Z. angew. Chem.*, **20**, 1217 (1907).

[2] *Ber.*, [1] **37**, 673 (1904).

[3] *Chem. Ztg.*, **36**, 165 (1912).

[4] *Ann. mines*, [5] **15**, 221 (1859).

[5] Ruff and Plato, *Loc. cit.*

[6] Wolter, *Ibid.*

[7] Fremy, *Ann. phys.*, [3] **47**, 5 (1856); Gore, *Phil. Trans.*, **1869**, p. 173. See also *Monatsh.*, **28**, 297 (1907), for the use of copper vessels in preparing the anhydrous acid.

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apparatus being of course surrounded with a freezing mixture. The copper vessel *C*, which was designed by Dr. G. A. Hulett, was found to be particularly useful in collecting and storing the anhydrous acid. It is a seamless copper cylinder with the ends and delivery tubes, also of copper, brazed in. The working portions of the valves are of copper, the remainder of brass. The entire interior of the vessel was given a heavy coat of electrolytic copper to prevent contact of the acid with the brazed portions. A copper tube *D* containing calcium chloride served as a guard against moisture; at *C* a current of dry air could be introduced. The joints *a*, *a*, *a*, were made tight by a wrapping of thin copper foil which was covered by several turns of rubber dam; these joints were found quite serviceable, and only very slight leakage took place.

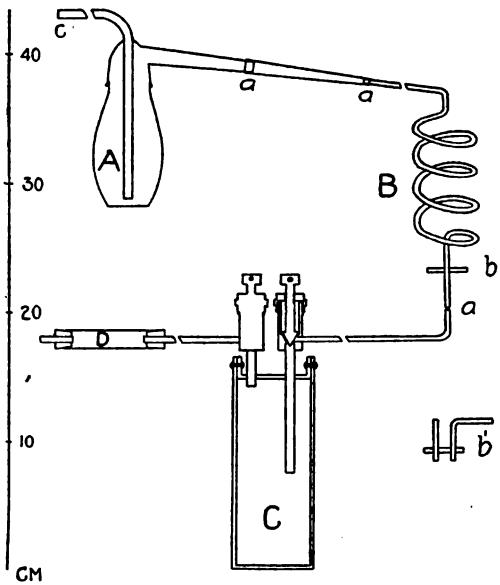

Fig. 1.

When sufficient acid (80 to 100 g.) had been collected, the copper vessel was put in the place of the retort, the lower pear-shaped part of the retort then being connected with the condenser by means of the brass stopper *b'*, which carried two copper tubes. The brass stopper *b'* was heavily coated with platinum black, and further protected from acid fumes by a piece of platinum foil. The acid was distilled by surrounding the copper vessel with water at 20° to 25°.

Preparation of Stannic Fluoride.—Sufficient hydrofluoric acid having been distilled into the retort, one-half of the theoretical quantity of anhydrous stannic chloride required was added,[1] and the retort quickly connected to the condenser by means of the straight tube of the stopper *b'*. This stopper fitted very tightly into the neck of the retort, but slight leakage occurred, which was reduced to a minimum by a seal of paraffin placed above the stopper. The reaction was allowed to continue at room temperature for 2 or 3 days, or at all events until hydrochloric acid ceased to be evolved, the condenser being continually surrounded with a freezing mixture. The platinum top of the retort was then fitted on, after

[1] The stannic chloride, prepared in the usual manner, was freshly distilled before using.

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which the excess of hydrofluoric acid was distilled off by careful heating, the temperature being gradually raised to 130°, at which temperature the decomposition of the compound SnF_4SnCl_4 commences. The heating was continued in a cautious manner until all stannic chloride had been removed. The temperature was then raised to about 700°, the stannic fluoride being sublimed and collected on the inner surface of a platinum crucible as shown in Fig. 2. The outside of this crucible was cooled with moist asbestos. The product condensed in beautiful white gleaming crystals. A Smith alkali-fusion crucible was found convenient as a container for the stannic fluoride until it was used, the crucible being placed in a desiccator over conc. sulfuric acid.

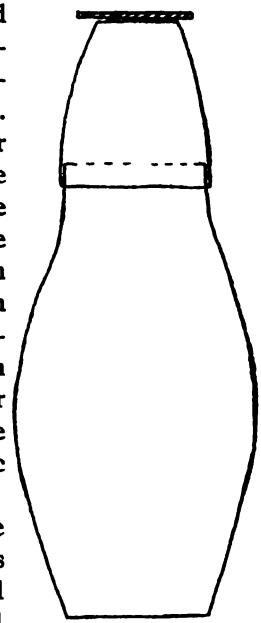

Fig. 2.

Weighed portions of the stannic fluoride were placed in a platinum crucible and the fluorine was expelled in the form of hydrofluoric acid by repeated evaporations with nitric acid, the tin being weighed as dioxide.

Sample taken. G.	% of tin found.	Calc. % of tin in stannic fluoride.
0.0956	61.6	61.03
0.1000	61.4	...
0.1107	60.8	...
0.7341	61.17	...

The Hydrolysis of Stannic Fluoride.

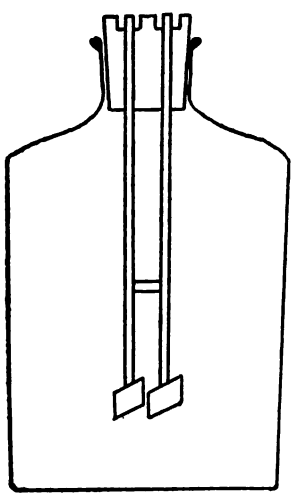

Fig. 3.

The hydrolysis of stannic chloride has been studied very successfully by the conductance method,[1] and it seemed reasonable to suppose that stannic fluoride could be studied in a similar manner. Weighed quantities of stannic fluoride were dissolved in conductivity water of specific conductivity 1.2×10^{-6} mhos, and weighed amounts of these solutions were placed immediately in a platinum conductivity bottle, Fig. 3. The electrodes were of the usual Ostwald type and the supporting wires, as well as the glass cross-piece, were coated with paraffin. The cell

[1] Wm. Foster, "The Hydrolysis of Stannic Chloride," *Phys. Rev.*, 9, 41 (1899); Kohlrausch, "Uber die durch die Zeit und durch das Licht bewirkte Hydrolyse einiger Chlorverbindungen von Platin, Gold und Zinn," *Z. phys. Chem.*, 33, 257 (1900).

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constant was frequently determined by means of 0.02 N potassium chloride solution, and remained the same, within the experimental error, during the course of the measurements. The conductivity apparatus was of ordinary precision. The cell was placed in a thermostat, which was maintained at a temperature of 25° ± 0.02°.

The conductivity changed rapidly at first, later becoming practically constant. The manner of the change may be understood from the following table, and the accompanying graphic representations of these results, which are plotted in Fig. 4:

TABLE I.—THE HYDROLYSIS OF STANNIC FLUORIDE SOLUTIONS.

Time from start of experiment.	Specific conductivity × 10^6 mhos.		
	Normality 0.0125.	Normality 0.013.	Normality 0.0155.
3 mins	748	...	...
5 mins	...	609	815
12 mins	765	...	...
20 mins	...	659	838
25 mins	773	...	...
30 mins	...	670	844
45 mins	...	...	849
50 mins	781	...	...
1 hr	...	695	858
3 hrs	...	...	888
4 hrs	816	...	...
6 hrs	833	...	899
12 hrs	859	...	...
24 hrs	867	793	941
48 hrs	880	798	959
144 hrs	...	834	974
216 hrs	...	...	974
480 hrs	...	880	...
600 hrs	...	890	...
624 hrs	...	890	...

In the case of stannic chloride, Foster found that it was not possible to follow the hydrolysis of solutions more dilute than 0.1 N by the conductance method, for equilibrium was established before the first conductivity reading could be made. Stannic fluoride plainly hydrolyses at a very much slower rate, for the change in conductivity of approximately 0.01 N solutions can be followed very easily by this method. The conductivity values obtained would seem to indicate a very slight initial dissociation of stannic fluoride into its ions.

The hydrolysis in these solutions is practically complete, and the final conductivity value is very closely that of a solution of hydrofluoric acid of the normality furnished by the decomposition of the stannic fluoride present in the sense of the equation

$$SnF_4 + 4HOH = Sn(OH)_4 + 4HF.$$

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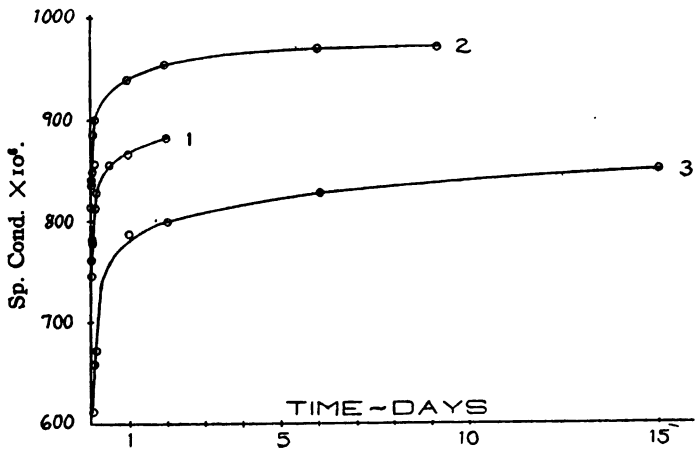
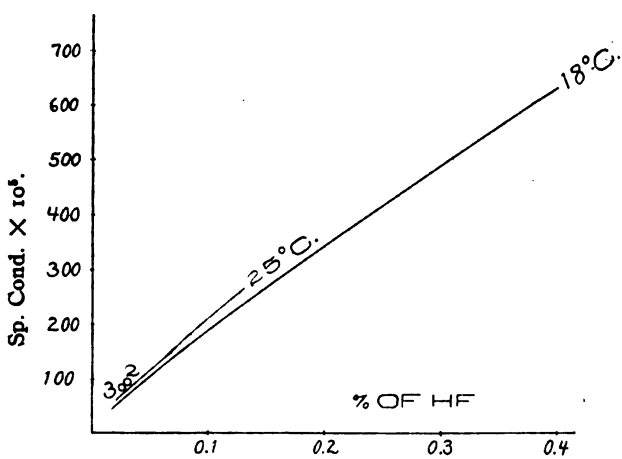


Hydrolysis of SnF_4.

Fig. 4.

The conductivity curve of hydrofluoric acid at 25°[1] is given in Fig. 5, together with the limiting conductivity values of Solutions 1 and 2.



Sp. Cond. of HF.

Fig. 5.

Prevention of Hydrolysis.—It seemed of interest to determine the minimum amount of hydrofluoric acid which would be needed to prevent tin from being precipitated by the hydrogen sulfide. For a solution containing 0.207 g. of tin per 100 cc., it was found that when hydrofluoric acid was present in the ratio

[1] Hill and Sirkar, "The Density and Conductivity of Solutions of Hydrogen Fluoride," *Trans. Roy. Soc. London*, **83**, 130 (1910).

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9 mols HF : 1 gram atom of tin.	Precipitation began after 5 minutes' passage of hydrogen sulfide.
10 mols HF : 1 gram atom of tin.	Precipitation began after 20 minutes.
11.5 mols HF : 1 gram atom of tin.	The solution remained perfectly clear for 35 minutes.
13 mols HF : 1 gram atom of tin.	The solution remained clear for 70 minutes, the passage of the gas being then discontinued.

It is necessary to have a sufficient concentration of hydrogen ions to prevent hydrolysis, as well as a suitable concentration of fluorine ions. The truth of the above statement is made evident by a consideration of the results of the following experiments:

The Effect of Hydrogen Sulfide on Solutions of Stannic Fluoride Containing Alkali Fluorides.—(1) A solution of crystallized stannic chloride, which contained 0.1 g. of tin per 100 cc. was treated with a solution of 4 g. of sodium fluoride made by neutralizing 48% hydrofluoric acid with sodium hydroxide. Hydrogen sulfide was passed through the solution for a long time. A whitish precipitate was formed, which gradually became yellow. The precipitate, after a thorough washing with water, alcohol, and finally carbon disulfide, was found to consist mainly of stannic oxide and sulfide.

A solution precisely similar to the above was made fairly acid with hydrochloric acid. Long passage of hydrogen sulfide gas through this solution did not occasion the slightest precipitation.

(2) Experiments similar to those described under (1) were made, using ammonium and also potassium fluoride. The results were in all respects similar to those described. In all cases the formation of the precipitate was sluggish, and in no case did the color of the precipitate reach that of pure precipitated stannic sulfide after a treatment of the solution with hydrogen sulfide lasting for 2 or 3 hours.

In his method for the separation of tin from antimony, McCay[1] recommends the use of sodium acetate to repress the dissociation of the hydrofluoric acid and thus make the precipitation of the antimonious sulfide more complete. Although the use of sodium acetate was later found to be unnecessary for the quantitative precipitation of the antimony,[2] it seems well to call attention to the fact that the conditions there recommended, namely, 0.2 to 0.5 g. of tin and antimony, 5 cc. of 48% hydrofluoric acid, in a volume of 300 cc., with the addition of 10 g. of crystallized sodium acetate, do not lead to the complete interaction of all of the hydrofluoric acid present with the sodium acetate to form sodium fluoride and acetic acid. If sufficient sodium acetate be added to react completely, stannic sulfide is precipitated when hydrogen sulfide is introduced, the

[1] THIS JOURNAL, 31, 375 (1909).

[2] *Ibid.*, 31, 381 (1909); 32, 1241 (1910).

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precipitation in all respects resembling that described under (1) and (2) above.

Discussion of Results.—It seems clear that the function of the hydrofluoric acid in the quantitative separations described is a double one—that it represses the dissociation of certain fluorides to such an extent that in several cases, as for example that of stannic tin, or tungsten, it is difficult or impossible to observe any of the reactions of the ions of these metals; further, that the acid supplies a sufficient concentration of hydrogen ions to prevent hydrolysis of the metal fluorides. There are at least two ways in which we might explain the apparent absence of the ions of these metals, when a suitable quantity of hydrofluoric acid is present. These different view-points may be illustrated by the facts relating to stannic fluoride, as follows:

(*a*) Stannic fluoride undergoes a slight initial dissociation into its ions, as indicated by its very slight conductivity. A suitable excess of hydrofluoric acid represses this dissociation to such an extent that none of the characteristic reactions of the stannic ion can be observed.

(*b*) Stannic fluoride may form a complex with the excess of hydrofluoric acid, of the general type H_nSnF_{4+n}. Any tendency of the complex to dissociate and give rise to the formation of ions of stannic tin, would be diminished or completely prevented by a sufficient excess of hydrofluoric acid.

The first explanation is simple and seems capable of accounting for all of the facts observed in working with hydrofluoric acid solutions of various metals.

The following are some objections which might be raised against the second explanation:

(1) An acid of the type mentioned, for example, H_2SnF_6, is certainly not stable in water solution, for solutions of stannic fluoride hydrolyze completely, in marked contrast to solutions of silicon tetrafluoride, which hydrolyzes partially to form silicic and hydrofluosilicic acids in the sense of the equation

$$3SiF_4 + 3H_2O = 2H_2SiF_6 + H_2SiO_3.$$

(2) Hydrofluoric acid solutions containing a known amount of stannic tin were neutralized with standard alkalies. The voltage change of a combination of the hydrogen electrode and 0.1 *N* calomel electrode was observed during this process. The containing vessel, and all glass tubes entering the solutions were protected from the action of the hydrofluoric acid by a coating of paraffin. The voltage readings were plotted against the cc. of standard alkali used. The curves obtained showed inflections only at the point where stannic hydroxide began to be precipitated, and that at which the precipitation was complete. These results would seem

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to indicate the absence of a complex acid, for Hildebrand and Bowers[1] were able to show the existence of halogen acids of zinc, of the type $HZnCl_3$, by this method, which they devised.

(3) The action of hydrogen sulfide on solutions of stannic tin containing large quantities of alkali fluorides seems to indicate that in this case, where we have ideal conditions for the formation of a complex, we are able to precipitate the tin practically completely, although slowly.

Summary.

Stannic fluoride has been prepared with a minimum use of platinum ware. Experiments have established the facts that this compound has a slight initial dissociation, as indicated by conductivity measurements, and that the compound hydrolyzes much less rapidly than does stannic chloride in solutions of the same normality.

Reasoning from the results of the experiments on the hydrolysis of stannic fluoride, and from facts encountered in other experiments with solutions of stannic fluoride containing alkali fluorides, or free hydrofluoric acid, there has been advanced a possible explanation of the mechanism whereby tin, and a number of elements which act in similar manner, in hydrofluoric acid solution, are prevented from being precipitated by various reagents.

The writer wishes to thank Dr. L. W. McCay for interest and guidance and to thank other members of the Chemical Department of Princeton University for valuable advice, during the progress of this work.

PRINCETON, N. J.

[CONTRIBUTION FROM THE LABORATORY OF QUALITATIVE ANALYSIS, COLLEGE OF THE CITY OF NEW YORK.]

THE DETECTION OF IODIDES IN THE PRESENCE OF CYANIDES.

BY L. J. CURTMAN AND C. KAUFMAN.

Received March 14, 1918.

The object of this investigation was twofold: first, to determine the extent of the interfering influence of cyanides in the test for iodides by the use of oxidizing agents; second, to provide a rapid and reliable method whereby one mg. of iodide could be detected in the presence of 500 mg. of cyanide.

Determination of the Amount of Interference.—In the presence of limited amounts of cyanide, iodine is visibly liberated by potassium nitrite as well as by other oxidizing agents. The reddish brown coloration which the liberated iodine imparts to the solution disappears, how-

[1] "A Study of the Action of Alkali on Certain Zinc Salts by Means of the Hydrogen Electrode," THIS JOURNAL, 38, 785 (1916).

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ever, after some time, the speed of disappearance varying with the amount of cyanide present. In connection with this observation, the following experiment is of interest: To a test tube were added successively one mg. iodine as potassium iodide, 0.4 mg. cyanide as potassium cyanide, 6 drops of 10% potassium nitrite, one cc. of starch solution and sufficient water to bring the volume up to 5 cc.; 4 drops of 10% hydrochloric acid were then added. At the same time 2 controls were run, one containing no cyanide and the other no iodide. In the tube containing both iodide and cyanide, a deep blue precipitate formed immediately on the addition of the acid. After some time, the blue color disappeared from all but a small portion that had settled to the bottom. On shaking slightly, however, the color entirely disappeared. The first control gave a deep blue permanent precipitate. The second remained colorless. It appears from these experiments, that although iodine may be visibly liberated in the presence of cyanide, it enters into combination again. In this connection it is of interest to note that the further addition of the oxidizing agent failed to liberate any iodine from the reaction mixture. A similar observation was made in attempts to liberate bromine by chlorine water in the presence of thiocyanate.[1]

Preliminary experiments to determine the amount of interference gave results which varied with the time which elapsed between the addition of the reagent liberating iodine and the shaking of the solution. The greater this interval, the smaller was the quantity of cyanide which prevented the detection of 1 mg. iodine. On the other hand, when the mixtures were shaken immediately after the addition of the oxidizing agent, closely concordant results could not be obtained; for these reasons a 5-minute interval was adopted.

A successful determination of the amount of interference was secured by the following procedure: From a graduated pipet, one cc. of standard potassium iodide solution (1 cc. = 1 mg. I) was introduced into a test tube. To this were added successively a definite volume of a standard potassium cyanide solution, one cc. of chloroform, 5 drops of 10% potassium nitrite, sufficient water to bring the volume to 5 cc. and 3 drops of 10% hydrochloric acid. The tubes were allowed to stand for 5 minutes and then shaken. The same procedure was followed to determine the interference of cyanides when hydrogen peroxide, potassium permanganate and chlorine water were, respectively, employed as iodine liberators. The results obtained are given in Table I.

The results of Table I clearly show that there is interference with each of the oxidizing agents tried and of these the interference is least with potassium permanganate.

[1] Curtman and Wikoff, THIS JOURNAL, 37, 299 (1915).

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TABLE I.—INTERFERENCE OF CYANIDES.

1 mg. I as KI; 1 cc. $CHCl_3$; 3 drops 10% HCl; Vol. 5 cc.

10% KNO_2,[1] 5 drops.		0.5% $KMnO_4$,[2] 2 drops.		Sat. Cl water, 2 drops.		2% H_2O_2, 5 drops.	
Mg. CN.	Test.	Mg. CN.	Test.	Mg. CN.	Test.	Mg. CN.	Test.
0.4	Neg.	30	Doubtful	20	Neg.	8	Neg.
0.3	Very faint	25	Very faint	10	Doubtful	7	Neg.
0.2	Fair	15	Faint	7	Faint	6	Faint
0.1	Good	10	Fair			4	Fair
		5	Good			1	Fair

Since in actual practice the reaction mixture is shaken immediately after the addition of the last reagent, the interference will not be as great as the above figures indicate. To form an idea of the interference in routine work, another set of experiments was run in which the solutions were shaken immediately after the addition of the potassium permanganate. Under these conditions, about twice as much cyanide is permissible.

Method for the Detection of Iodides in the Presence of Cyanides.—In a previous communication[3] from this laboratory, cobalt nitrate was successfully used to precipitate cyanides, ferrocyanides and ferricyanides, the well-known difficulties of filtration being surmounted by the addition of asbestos fiber. These features were embodied in the present method. The solution, the volume of which should be about 25 cc., is treated with an excess of cobalt nitrate solution.[4] After adding 3 g. of washed asbestos fiber, the mixture is boiled for one-half minute with stirring, and filtered. The precipitate is washed twice with small amounts of water; the filtrate and washings, after concentration by evaporation, to about 4 cc., are transferred to a test tube. The dish is rinsed with 2 cc. of water and the rinsings united with the solution in the test tube. The test for iodides is then made by adding 1 cc. of chloroform, 2 cc. 3 *N* sulfuric acid and 2 drops of 0.5% potassium permanganate. A violet color in the chloroform layer, after shaking, proves the presence of iodide. The following test analyses show the method to be reliable:

TEST ANALYSES.

Anal. No.	Mg. CN.	Mg. I.	Result.
1–5	500	0.0	Negative
6–10	500	1.0	Positive

Summary.

1. A study has been made of the interference of cyanides in the test for iodides.

2. Data are supplied showing the extent of the interference when ni-

[1] In these experiments the HCl was always added last.

[2] 2 cc. 3 *N* H_2SO_4 were used in place of 3 drops of dil. HCl.

[3] Curtman and Harris, THIS JOURNAL, 38, 2625 (1916).

[4] This solution contained 25 g. $Co(NO_3)_2.6H_2O$ in 100 cc.

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trite, hydrogen peroxide, saturated chlorine water and potassium permanganate are, respectively, used to liberate the iodine.

3. A rapid and reliable method is proposed which is capable of detecting one mg. iodine as iodide in the presence of 500 mg. of cyanide.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WISCONSIN.]

A STUDY OF THE CHEMISTRY OF GOLD AT HIGH TEMPERATURES AND PRESSURES.[1]

BY HAROLD H. MORRIS.

Received April 2, 1918.

This contribution to the chemistry of gold is the result of one of a series of investigations undertaken in the chemical laboratory of the University of Wisconsin on the deposition and alteration of various minerals due to the effects of heat and of aqueous vapor pressure. A particular study was made of the compounds of gold because of the relation of such a study to the theories concerning the deposition of gold in nature.[2]

The apparatus used here is described in detail, since it is expected that only slight modifications will be necessary in carrying on further work in this field. It consisted of an electrically heated steel bomb, and a platinum platinum-rhodium thermocouple used in connection with a potentiometer for temperature measurements.

The steel bomb was of the general type of the Morey bomb,[3] the several parts of which are shown in cross section in Fig. 1, which is drawn to scale. The material used in the construction was electric chrome-vanadium steel. The three principal parts of the bomb are A, B and E. The body

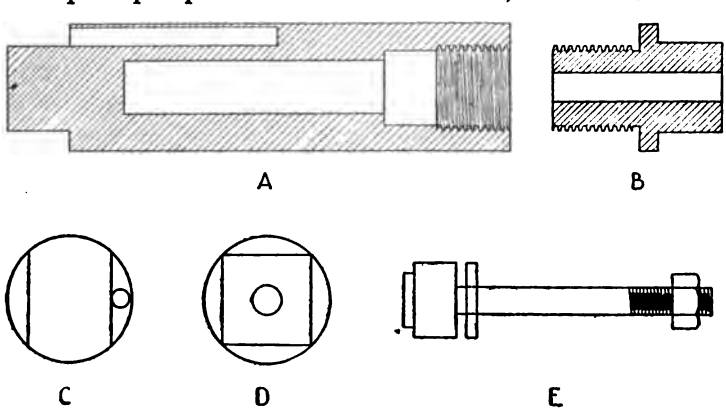

Fig. 1.

[1] A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Lenher and Morris, *Econ. Geol.*, [3] 13, 161.

[3] Morey, THIS JOURNAL, 26, 215 (1914).

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of the bomb A consisted of a cylinder 3 inches in diameter and 12 inches long. The two sides of the bottom were squared off for 1.5 inches so that it might be set in a steel plate having a corresponding opening. This plate was fastened to the floor and acted as a vise. The bottom of the bomb is shown in C. A hole $^7/_{16}$ inch in diameter and 5 inches deep in the wall of the bomb A and C, provided a place for the thermocouple which was encased in a quartz tube.

The chamber in the center of the bomb where the reactions were carried on was $6^3/_8$ inches deep, and $1^1/_4$ inches in diameter. Closure was effected by the parts shown in B and E. The end of the plunger fitted tightly into the top of the central chamber shown in A, while a copper gasket $^1/_8$ inch thick rested on the seating immediately above. The stem of the plunger, $^5/_8$ inch in diameter, moved easily through the opening in the plug B, $^3/_4$ inch in diameter, and was held in place by a nut at its outer end. The cylindrical portion in A corresponding to the end of the plunger was made with a 5° taper so that a slight loosening of the plunger allowed it to move freely. The plug B was provided with an Acme thread of 8 turns to the inch. The top of the plug was cut down to a square $2^1/_8$ inches on a side, a top view of which is shown in D. The object of constructing the cap of 2 pieces was to avoid turning the copper gasket on the seating either during the opening or closing of the bomb. Such tendency toward turning as resulted when the plug was tightened was obviated by inserting an iron washer between the top of the plunger and the bottom of the plug. When the bomb was opened the small nut at the end of the plunger was first loosened, then as the plug was turned out it exerted a straight pull on the plunger, which brought the copper gasket out with it. A 36-inch spanner wrench was used for removing the plug.

The heating furnace was constructed of a piece of 3-inch iron pipe 20 inches long, attached firmly to a circular piece of sheet iron 10 inches in diameter, the edges of which were turned up at right angles so that it could be bolted to the sheet iron jacket which surrounded the whole. The pipe was covered with alundum cement, dried, and wound with No. 18 nichrome wire, the terminals being carried out at either the top or the bottom of the furnace. A 10-inch cylinder of sheet iron 20 inches long was placed around the pipe and bolted to the sheet iron plate at the bottom. This jacket was filled with finely powdered magnesium oxide and asbestos, and a cover bolted into place. Two short pieces of $^3/_8$-inch pipe provided with caps fastened to the sides of the jacket slightly above the center, rested in supports as indicated in the diagram, and permitted the furnace to be rotated to any angle. The lower end of the 3-inch pipe was covered by a cap screwed to the bottom of the furnace. A small hole was cut through this cap to allow introduction of the thermocouple.

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Above the cap was placed a plug of asbestos about 3 inches deep so that the bomb, when in place, would be in about the center of the furnace, and so be more evenly heated.

The heating of the furnace was controlled by means of a rheostat. The wiring of the switchboard used in connection with the furnace is shown in Fig. 2. The light A indicated whether or not current was on the line. The fuse plugs C and D were provided with 15-ampere fuses. The resistance wire in the rheostat was No. 18 nichrome wire in one-foot sections. The light B was connected so that it would burn when the switch E was opened, provided the heating coil in the furnace

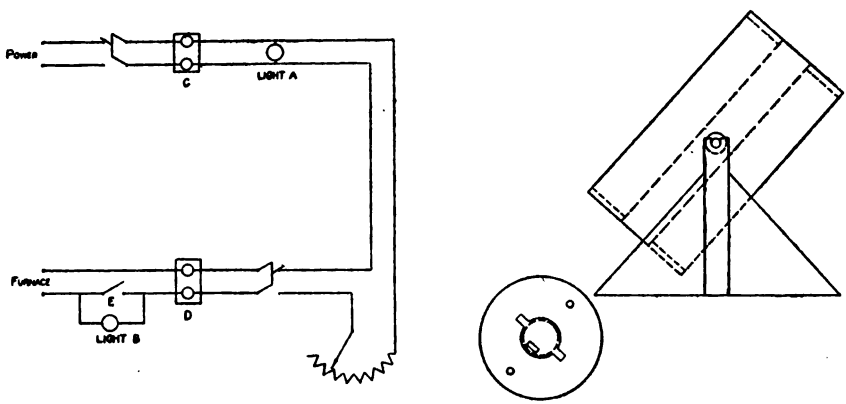

Fig. 2.

was intact, and it also served as an additional heat control. The current delivered at the board was from a 110-volt alternating circuit. The junction of the thermocouple was encased in a quartz tube and inserted through the lower end of the furnace into the opening provided for it in the steel bomb. The outer ends of the couple were connected by means of copper wire to the potentiometer, the junction of the wires being maintained at 0°.

Standardization of Apparatus.

Two standardized thermocouples were recalibrated using boiling naphthalene and boiling sulfur. The curves accompanying the instruments were found to be correct.

One couple was placed in position in the bottom of the bomb, and the other was placed inside the bomb. Simultaneous readings were taken throughout the range of temperatures to be used. It was found that the difference in temperature between the couple in the bottom of the bomb and the one inside the bomb did not exceed 5°, which was about the limit of accuracy of the temperature reading as a whole.

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Method of Experimentation.

The general method of performing the experiments was as follows: The inside of the bomb was thoroughly cleaned with a brush and distilled water. The solutions or materials to be used were placed in a quartz tube, which was covered with a quartz crucible, and lowered into the bomb by means of a platinum wire. Sufficient water was added to fill the compartment about one-half full outside of the test tube, which was always an excess. Before the cover of the bomb was screwed into place the thread was covered with graphite; this aided in making the bomb tight, and yet facilitated the removal of the top as it did not become rusted in. The experiments usually required about 24 hours for completion. After heating for the desired length of time the current was shut off and the bomb allowed to cool slowly in the furnace.

Preparation of Materials.

The water used in all experiments was first distilled from sodium hydroxide and potassium permanganate, and then from sulfuric acid and permanganate in order to free it from all organic reducing materials.

Gold hydroxide was prepared in the following manner: Pure gold hydroxide was dissolved in water, filtered through an asbestos felt, and the gold precipitated by passing in sulfur dioxide. The gold was collected, washed thoroughly, and melted into a small button. This was dissolved in aqua regia and the nitric acid removed by repeated evaporation in the presence of hydrochloric acid. The resulting gold chloride was dissolved in water, and after standing a few hours the solution was filtered through an asbestos felt and the gold re-precipitated with sulfur dioxide. The process of separating the gold, washing, melting, etc., was repeated, and when the clear solution of gold chloride was again obtained it was warmed and an excess of pure magnesium oxide added. The resulting precipitate of a mixture of gold hydroxide and magnesia was washed by decantation until the washings gave no further test for chlorides with silver nitrate. The magnesia was then extracted by treatment with warm dil. nitric acid. Lastly, a treatment with warm conc. nitric acid, followed by washing till the wash water contained no magnesium, gave pure gold hydroxide. This material, when dried on a steam bath to a dark brown powder, was readily and completely soluble in cold hydrochloric acid.

Experiments with Gold Hydroxide.

In some preliminary experiments performed in this laboratory by Mr. W. G. Crawford[1] on the decomposition of gold oxide by heat under the pressure of aqueous vapor, it was found that the oxide decomposed completely at 315°. Below that temperature a lighter yellow material formed in part, but on treatment of this whole residue with boiling conc. hydro-

[1] Unpublished notes.

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chloric acid it was noticed that the red-brown oxide dissolved at once, while the lighter material dissolved more slowly, but completely.

Boiling conc. hydrochloric acid was used as the reagent to determine whether the oxide had been completely decomposed, working on the supposition that the undecomposed oxide would dissolve, leaving insoluble such metal as had been formed. In this latter work it soon appeared that this was not a sharp separation, since small amounts of gold were easily dissolved in the presence of an excess of the oxide, which at once became auric chloride on treatment with hydrochloric acid, and it was only when decomposition had gone on to a very marked extent that the gold remained insoluble.

It was found that the solvent action of auric chloride and hydrochloric acid on metallic gold takes place with the formation of aurous chloride, and further that the aurous chloride may be titrated with potassium permanganate using preventative solution.

In a series of experiments in which a few milligrams of gold hydroxide were heated with water in a quartz tube a slight reduction to metal was obtained at 274–279°. Incomplete reduction was obtained by heating 14 hours to 300–310° and by heating 10 hours at 315–321°; 13.5 hours at 318–322° gave complete reduction to metal.

One preparation of gold hydroxide gave partial decomposition as low as 135° and complete reduction at 260° by 5 hours' heating. In some cases this material gave yellow solutions containing gold. This marked lowering of the decomposition point of gold hydroxide was evidently due to the presence of small amounts of inorganic salts, since the addition of a trace of magnesium chloride to the gold hydroxide and water, with subsequent heating to 264°, gave a distinctly yellow solution containing gold, while beautifully crystallized gold appeared in the bottom of the tube. Slightly larger amounts of magnesium chloride gave gold in solution but with the difference that no free metal was obtained. This solution, after standing in the air for a short time, precipitated a mirror of gold on the sides and bottom of the beaker.

In view of the fact that crystalline gold was obtained when small quantities of magnesium chloride were used, and no free metal appeared when the concentration was increased, it appeared that magnesium chloride might be a solvent for gold at high temperatures, depositing the gold in the crystalline form as the solution became saturated on cooling. It was found, however, that magnesium chloride solution at 260–270° exerted no solvent action on gold leaf.

Sodium chloride in small amounts heated with gold oxide to 260–268° gave gold in solution and a precipitate of metal. In this case the metal was spongy, quite different from the well-formed crystals obtained when magnesium chloride was used.

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Calcium chloride and gold hydroxide were heated together to 281°, 292°, 322° and 353°. In each case yellow gold-bearing solutions were obtained, together with a light yellow residue. Only at the temperature of 353° with 15% calcium chloride was there a slight reduction to metal.

The yellow residue was washed free from soluble chlorides, and on treatment with nitric acid it took on the dark reddish brown color characteristic of gold hydroxide. The nitric acid was decanted and found to be free from calcium and chlorine. The residue on solution in hydrochloric acid showed no calcium. The calcium chloride had no other effect on the hydroxide than to prevent its reduction to metal and to change its color to a light yellow.

It is interesting to note that under these conditions sodium and magnesium chlorides readily cause the reduction of the gold to metal, while in the work of Diemer[1] on the reduction of auric chloride to aurous chloride by sulfur dioxide in the presence of alkali chlorides, it was shown that sodium chloride and magnesium chloride were most effective in preventing complete reduction, while calcium chloride was the least effective.

In each of these experiments the yellow solutions obtained were reduced to metallic gold on standing in the air, the gold forming a mirror on the walls of the container.

Experiments with Calcite and Gold Chloride.

The gold chloride used in these experiments was made by dissolving gold hydroxide, prepared as previously described, in hydrochloric acid, the very slight excess of acid in the clear solution being neutralized with calcite. When effervescence had ceased the quartz tube containing crystals of calcite and the gold chloride solution was placed in the bomb and heated.

A series of experiments at various temperatures yielded the following facts: The first step in the reaction of gold chloride and calcite is the formation of gold hydroxide, but at higher temperatures the hydroxide is decomposed giving free gold.

At 279° much of the gold present was converted to hydroxide which adhered to the surface of the calcite. Very little metal was formed at this temperature. Undecomposed hydroxide was found up to 312°, but the amount of free metal continually increased with rise of temperature. At 310° it was found possible to grow crystals of gold on the surface of the calcite. These crystals were in forms belonging to the isometric system. At 320° the surface of the calcite became almost entirely covered with a plating of gold with the characteristic bright yellow color, but no crystals were visible in the coating even when highly magnified.

[1] Diemer, THIS JOURNAL, 35, 552 (1913).

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At 327° the gold plating began to show well-formed crystals of gold adhering to it. Temperatures of 330–337° gave complete reduction of the gold in solution to metal. The gold appeared entirely in the crystalline form except that portion which formed the plating on the surface of the calcite. Nearly all of the crystals adhered to this metallic coating.

The best plating and crystal formation on the surface of the calcite was produced by raising the temperature to 330° for a time, then lowering it to 320–325°. The higher temperature gave a reduction to metal, while the lower temperature maintained for some hours promoted crystal growth.

A solution of gold chloride distinctly acid with hydrochloric acid was heated with calcite to 324°. Gold was precipitated but the calcite was not plated. At the end of the heating the solution was still strongly acid so that when pressure was released in the bomb, effervescence immediately recommenced.

Fig. 3 shows a crystal of calcite from Cumberland, England, which was heated for 3 hours to 300°, and during a few minutes to 358°, in the presence of strong gold chloride solution. Slight plating resulted. It was returned to the bomb with fresh gold chloride solution and heated for a day, reaching a maximum temperature of 343° without materially improving the plating. On heating for 2 days longer, reaching a maximum temperature of 347°, the plating shown in Fig. 3 resulted.

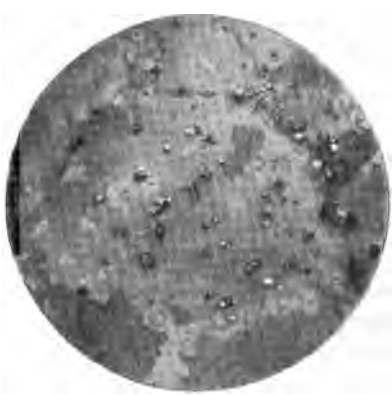

Fig. 3.

Some very strong gold chloride solution was prepared by saturating conc. hydrochloric acid with gold hydroxide. This gave a solution which was acid to litmus but which did not effervesce with calcite. On heating a piece of calcite with this solution for 2 days to a maximum temperature of 334° all the gold was removed from the solution and the calcite was found to be thickly covered with a bright yellow pulverulent coating containing a few bright crystals of metal. A second experiment, using the same materials and heating for one day to 336°, gave exactly similar results.

In these experiments the strength of gold chloride solution used produced a rather high concentration of calcium chloride. This salt appeared to exert a stabilizing action on the gold hydroxide, and the plating out of metallic gold was prevented. This same behavior is possible when a strongly acid gold chloride solution is heated with calcite, forming calcium chloride during the neutralization, and explains many unsuccessful

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attempts to obtain well plated calcite in solutions of more than moderate concentrations of gold chloride.

Magnesite and gold chloride solution at 322° gave crystals of gold on the surface of the magnesite, but in this case the crystals were fern shaped, appearing under the microscope as elongated crystals twinning to form strands and filaments. Magnesite and gold chloride heated to 332° gave good gold plating on the magnesite, but again the crystals adhering to this coating took the form of long threads, instead of the perfect cubes and octahedra such as were obtained on calcite.

Under the varying conditions of the many experiments performed on gold solutions, crystals of gold of various habits were produced. In some cases the crystals appeared as thin plates in the shape of perfect triangles, hexagons, or polygons; again long threads, in some cases over an inch in length, were produced. These always appeared under the microscope as composed of many crystals grown end to end. Cubes, tetrahedra, and many combinations of the forms of the isometric system were very common. In general, it may be said that whenever the gold was deposited from solutions by heat and pressure it was crystalline, showing more or less perfect forms.

Gold Chloride and Alkali Chlorides.

A series of experiments was next undertaken to determine the temperature at which gold chloride would decompose when heated under the pressure of aqueous vapor, and also the effect of the presence of alkali chlorides on this decomposition point.

Several preparations of gold chloride which were slightly acid to litmus were heated to the critical temperature of water, 365–372°, without decomposition. At the end of the experiments no free metal was found, and no change in the appearance of the solution was noted. Slightly higher heating (379°) gave complete reduction, the metal appearing in the crystalline form.

The crystals in this case were especially fine and of a great variety of form. Some practically perfect octahedra were produced, as well as chains of crystals. In other experiments where the gold chloride was heated to 400°, 435° and 445° complete reduction was obtained in each case. The experiment at 445° gave fern-shaped crystals as much as one-half inch long.

The work of Cailletet and Coloradeau[1] gives the critical temperature of water as 365°. In the present work it was found that gold chloride was stable up to a temperature of 372°, but was decomposed at 379°. There appeared to be some relation between the critical temperature of water and the decomposition of gold chloride, which was substantiated

[1] Cailletet and Coloradeau, *Compt. rend.*, 106, 1489 (1888).

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by the work of Holborn, Henning, and Baumann,[1] who give the critical temperature of water as 374°.

After having determined the stability of gold chloride, the effect of the addition of small amounts of alkali chlorides was next investigated. In the first of these experiments one small crystal of calcium chloride was added to 10 cc. of gold chloride solution, and the mixture heated to 352°. A few small crystals of gold resulted. The same solution was again heated, this time to 387°, but no further reduction took place. Gold chloride solution containing 10% calcium chloride was heated to 404° for nearly a day without the slightest reduction to metal being obtained. Gold chloride containing 8% calcium chloride was heated for an equally long time to 454°, and in this experiment a few small crystals were obtained.

From these experiments it is evident that if sufficient calcium chloride is added a solution is obtained which may be heated nearly a hundred degrees above the critical temperature of water before decomposition starts.

Gold chloride solution containing 8% magnesium chloride gave no reduction to gold at 383°, while the same solution heated to 454° showed incipient reduction to metal.

A gold chloride solution containing 8% sodium chloride heated to 460° showed no reduction to metallic gold in the solution. At the very top of the tube an inch and a half above the solution some strands of metallic gold had formed which extended directly across the tube, a distance of nearly an inch. Under the microscope these strands appeared to consist of many small crystals attached end to end. On allowing this solution to stand in the air, gold crystallized out on the sides of the tube. It is characteristic of all of these solutions that after heating they precipitated a mirror of gold on the walls of the containing vessel if allowed to stand in the air, but in this case the gold appeared as well-formed crystals.

The solutions obtained in these experiments were separated from the metallic gold and reheated. Heating to a temperature of 504° gave no further reduction to metal.

Following the investigation of the stability toward heat of the double chlorides of gold with those of sodium, calcium and magnesium, a series of experiments was undertaken which had for its object a study of the deportment of these double chlorides with calcite and magnesite. In detail these experiments were as follows:

Gold chloride containing 8% sodium chloride when heated with calcite to 347° caused the calcite to become fairly well covered with small crystals of gold. Solutions of the same strength heated to 399° gave only a few flakes of gold in the tube. These flakes were in the form of thin plates, some triangular, others hexagonal or polygonal.

[1] Holborn, Henning, Baumann, *Ann. phys.*, 31, 945 (1910).

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Since sodium chloride solution under pressure is a solvent for gold,[1] it is not surprising that no great amount of metal separates under the above conditions.

A gold chloride solution containing 8% sodium chloride and a piece of magnesite was not changed by heating to 336°, the solution at the end appearing exactly as it had at first. This same solution with magnesite heated to 490° gave only a very few crystals of gold on the magnesite.

Fig. 4.

Calcite when heated to 444° with gold chloride solution containing 8% of magnesium chloride gave nearly complete reduction to metal. The calcite was not plated with the gold. The metal appeared as exceptionally beautiful fern-shaped crystals. Two of these crystals are shown in Figs. 4 and 5.

A series of experiments was next performed in which calcite was heated with a saturated solution of silver chloride in saturated sodium chloride solution, to which was added gold chloride saturated with sodium chloride. In these experiments gold crystals were obtained on the calcite at temperatures as low as 322°. The gold was free from silver, the latter apparently remaining entirely as chloride. Heating to a temperature of 465° failed to give any metallic silver or a silver-gold alloy.

Calcium bicarbonate solution when heated with gold chloride had no effect on the rate of decomposition of the chloride. The solution showed practically no reduction below, and complete reduction above the critical temperature of water.

Magnesium bicarbonate, on the other hand, heated with gold chloride to 348°, gave a complete precipitation of the gold from solution. The gold appeared for the most part as crystals of the metal, but there was also present a small amount of hydroxide.

Fig. 5.

[1] Lenher, *Econ. Geol.*, 4, 562 (1909).

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Summary.

A steel bomb for work at high temperatures and pressures is described. The details of construction of an electric furnace for heating the bomb are given.

Gold is soluble in auric chloride which is acid with hydrochloric acid at the boiling temperature. Aurous chloride is formed, which may be titrated with potassium permanganate.

Pure gold hydroxide when heated with water in a closed bomb is decomposed, yielding metallic gold, at 322°.

Small quantities of inorganic salts lower this point of decomposition as much as 70°. Magnesium chloride and sodium chloride act in this way, while calcium chloride has a slight tendency to prevent decomposition.

Calcite when heated with gold chloride under pressure becomes plated with gold above 310°. Excellent gold crystals may be obtained as part of the gold plating. The reaction goes on in two steps, the first step being the formation of auric hydroxide, while the second is the reduction of the hydroxide to metal.

Magnesite heated with gold chloride under the same conditions may be gold plated. The crystals formed in this case show a different crystal habit from those obtained on calcite.

Gold chloride may be heated under the pressure of aqueous vapor as high as the critical temperature of water before metallic gold is caused to separate.

Gold chloride solution to which has been added small amounts of sodium chloride, magnesium chloride, or calcium chloride, is much more stable toward heat than gold chloride solution alone, only incipient reduction being obtained at 450–460°.

The stability of these double chloride solutions is also exhibited toward calcite and magnesite, which only became slightly plated with metallic gold when heated to 500°.

Calcium bicarbonate has no effect on the stability of gold chloride toward heat.

Magnesium bicarbonate acts like the normal carbonate when heated with gold chloride, causing the formation of gold hydroxide and metal at 322°.

This investigation was undertaken at the suggestion of Professor Victor Lenher, and I take this opportunity of expressing my deep appreciation of his advice and encouragement which have been so helpful both in the laboratory and in the classroom.

MADISON, WISCONSIN.

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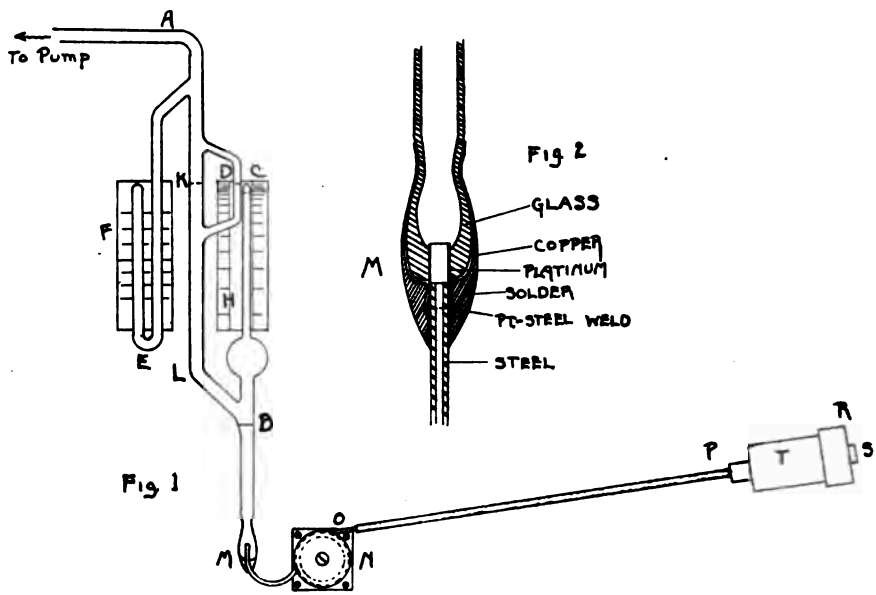
NOTES.

A Simplified Short Vacuum Gauge.[1]—A modified short Gaede gauge[2] has been described by me, in which all rubber connections are eliminated by the use of a ground-glass joint to connect the adjustable mercury reservoir to the evacuated space. This type of gauge has given excellent service over intervals of time limited only by accidental breakage of glass parts. The purpose of this note is to show how a gauge may be constructed along similar lines without the use of a ground-glass joint. This is accomplished by connecting the mercury reservoir T, Fig. 1, to the vacuum system AB by means of a small steel tube MR, which is coiled several times around a cylinder N just before entering the glass tube at M. The



reservoir T is a steel cylinder with thin walls, of sufficient capacity to fill the system BK when the arm OR is inclined at an angle of 60° with its resting position. At S is an opening to facilitate the filling and adjusting of reservoir and tube, and is securely closed by means of a screw.

The coil of steel tube is anchored to the cylinder N, or axis of the coil, at the glass end, to avoid strains in the glass parts when the arm is moved. The portion OP of the arm supporting the reservoir is made of larger steel tubing, with inside diameter 4 mm. and with thin walls; this is to give greater rigidity to the arm and greater speed in operating the gauge.

The manner of connecting the steel tube to glass tube is shown in Fig. 2. The union is easily effected by means of a small, hollow platinum

[1] Communicated by the manager.

[2] *Phys. Rev.*, 6, 51 (1915).

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cylinder which may be welded to the steel tube and fused into the glass tube. When such a platinum cylinder is lacking, platinum foil may be utilized as in the present case. When the tube made of foil is welded to the steel tube and fused into the glass tube, the latter is silvered and copper-plated. The seam in the platinum tube may then be rendered gas-tight by a layer of solder bridging the copper-plated glass surface and the surface of the steel tube.

The dimensions and operation of the gauge are the same as in the former one. The dimensions of the metal parts are as follows:

N — Metal axis 3 cm. diameter.
OP — 30.2 cm. long, 5 mm. outside diameter.
OM — Coil of steel tubing $^1/_8$ inch outside diameter, $^1/_{16}$ inch inside diameter, 30 inches long, wound on axis *N*.
T — 3.3 cm. diameter.
R — 3.7 cm. diameter.
PS — 9.5 cm. long.

This manner of connecting a mercury reservoir to a glass chamber may be of value in other pieces of apparatus where pressure or volume is required to be adjustable.

ENOCH KARRER.
PHYSICAL LABORATORY OF THE UNITED GAS IMPROVEMENT CO.,
PHILADELPHIA, PA.

An Improved Form of Thermo-regulator.—The form of thermo-regulator shown in Fig. 1 has been used by the writer for 3 years and found to be very satisfactory. The essential feature is that the adjustments are made by means of a plunger and plunger tube which regulate the height of the mercury with respect to a *fixed* platinum wire.

The apparatus as shown in the cut is made entirely of glass with the exception of the two brass tubes and screws on the plunger and plunger tube, the brass clips (Fahnestock spring binding posts) holding 2 of the wires, and the 3 connecting wires. The brass parts improve both the efficiency and the appearance of the regulator, but are not essential. They may be replaced by a rubber stopper cut out as shown in Fig. 2. The stopper is necessarily cut so as to fit

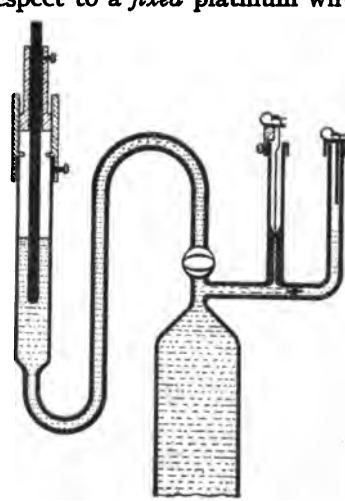

Fig. 1.

Fig. 2.

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the plunger and the plunger tube tightly, else the plunger will not remain in the proper place. The coarse adjustment with such an arrangement is best made by moving the plunger through the stopper, and the fine adjustment by turning both the stopper and plunger, applying at the same time a gentle pull or push. This simple modification of the apparatus is given since the brass attachments are not always readily obtained and are troublesome to make.

The use of a fixed platinum wire has its advantages. Great care need not be taken in the centering of the platinum wire, for if after the wire has been soldered to the cap it is found to be off center, simple bending, as shown in the figure, will remedy this. In the ordinary regulator the electrical connection between the movable platinum wire and the binding post is made through a screw and nut. When the threads become worn or corroded this connection often becomes uncertain and may give rise to considerable trouble. With a fixed wire it is possible to solder the wire, cap and binding post together, thus eliminating any such source of trouble.

JOHN B. FERGUSON.

GEOPHYSICAL LABORATORY,
CARNEGIE INSTITUTION OF WASHINGTON,
WASHINGTON, D. C.

ON SOME HALOGEN DERIVATIVES OF AROMATIC AMINES AND THEIR ANALYSIS. I.[1]

BY F. B. DAINS, T. H. VAUGHAN AND W. M. JANNEY.

Received January 9, 1918.

In the course of the study of the effect of the halogens on the reactivity of the aromatic amines, it became necessary to prepare certain iodine substitution products of these amines, and the following paper contains some results of this phase of the work. Hofman[2] showed that aniline reacted directly with iodine yielding *p*-iodoaniline. Later Wheeler[3] and his students investigated the action of iodine on the toluidines and found that substitution products were easily obtained. Our experiments indicate that the chloro- or bromo-substituted anilines are capable of reacting in an analogous fashion with the formation of chloroiodo and bromoiodo derivatives.

The Introduction of Iodine into the Bromoanilines.

Preparation of 4-Bromo-2-iodoaniline.—The general procedure of Wheeler was followed with satisfactory results. A mixture of 25 g. of 4-bromoaniline and 37 g. of iodine was heated under a reflux condenser with 18 g. of pure calcium carbonate, 60 cc. of ether and 60 cc. of water.

[1] Owing to the departure of two of the authors, the investigation, though incomplete, is published. The work will be continued in this laboratory.

[2] *Ann. chim.*, **67**, 61 (1848).

[3] *Am. Chem. J.*, **42**, 441, 448 (1909); **44**, 127, 500 (1910).

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After several hours the iodine disappeared and a black oily product which solidified on cooling settled to the bottom of the flask. The black solid is soluble in ether, alcohol, benzene and gasoline. It is best purified by solution in dilute alcohol, from which it can be obtained, after repeated crystallization, in fine white needles, melting at 71°.

Calc. for C_6H_5NBrI: N. 4.71. Found: 4.76, 4.69.

That the iodine atom is in the 2-position is proved indirectly by the fact that this substance is different from the only other possible isomer, namely the 4-bromo-3-iodoaniline, which had been previously obtained by Wheeler and Valentine.[1] Other evidence is the following: The above aniline was diazotized and the amine group removed. The resulting bromo-iodobenzene gave on nitration yellow crystals melting at 85°, corresponding to the 4-bromo-2-iodo-1-nitrobenzene.

Derivatives of 4-Bromo-2-iodoaniline.—The hydrochloride prepared from the aniline dissolved in benzene, and dry hydrogen chloride, melts at 205–6°.

Calc. for $C_6H_5NBrI.HCl$: HCl, 10.70. Found: 10.90.

Acetic anhydride readily gives the acetanilide in the form of fine, white crystals from alcohol with melting point of 148°.

Calc. for C_8H_7ONBrI: N, 4.11. Found: 4.36, 4.44.

The benzoyl derivative is soluble in hot alcohol and melts at 152°.

Calc. for $C_{13}H_9ONBrI$: N, 3.48. Found: 3.61.

No formamidine was obtained when the aniline was heated with orthoformic ester at 120–30°.

4-Bromo-2-iododiphenylthiourea from phenylmustard oil and the aniline separates from alcohol in fine, white, hair-like crystals, melting at 167°.

Calc. for $C_{13}H_{10}N_2SBrI$: N, 6.46. Found: 6.51, 6.68.

Allyl-4-bromo-2-iodophenylthiourea forms flaky, silver-white crystals from alcohol, melting at 177°.

Calc. for $C_{10}H_{10}SBrI$: N, 7.05. Found: 7.26.

4-Bromo-2-iodophenylurea results when the aniline and potassium cyanate are heated in glacial acetic acid solution. It is only slightly soluble in water, but can be crystallized from alcohol. Its melting point is 167°.

Calc. for $C_7H_6ON_2BrI$: N, 8.21. Found: 8.04.

Anisal-4-bromo-2-iodoaniline from anisic aldehyde and the aniline on warming; strongly refracting crystals from alcohol, melting at 118°.

Calc. for $C_{14}H_{11}ONBrI$: N, 3.36. Found: 3.61.

Cinnamal-4-bromo-2-iodoaniline is soluble in alcohol, ether, gasoline and benzene, and melts at 96°.

[1] *Am. Chem. J.*, **22**, 275 (1899).

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Calc. for $C_{15}H_{11}NBrI$: N, 3.40. Found: 3.38.

The piperonal 4-bromo-2-iodoaniline melts at 120°.

Calc. for $C_{14}H_9O_2NBrI$: N, 3.25. Found: 3.48.

The *o*-nitrobenzal-4-bromo-2-iodoaniline has a melting point of 159°.

Calc. for $C_{13}H_8O_2N_2BrI$: N, 6.50. Found: 6.30.

Preparation of 4-Bromo-2,6-diiodoaniline.—When *p*-bromoaniline is treated with 2 molar weights of iodine, as in the previous experiment, a black solid is obtained, which dissolves readily only in warm pyridine. Water precipitates a product which, by treatment with alcohol, can be separated into 4-bromo-2-iodoaniline and 4-bromo-diiodoaniline. This latter, by repeated crystallization, was obtained as a white solid melting at 148°. The diiodo compound is formed also by the action of iodine (one mol.) on the bromoiodoaniline.

Calc. for $C_6H_4NBrI_2$: N, 3.30. Found: 3.34.

In the bromodiiodoaniline, the second iodine atom is probably in the 6-position. The compound possesses little basic properties, since in benzene solution it failed to form a hydrochloride.

Preparation of 3-Bromoiodoaniline.—From *m*-bromoaniline and iodine there was obtained an oil volatile with steam, which solidified only after 2 months' standing in a desiccator. It then melted at 56°. The compound itself was not analyzed, but the oil first obtained was converted into its hydrochloride, which melts at 192°.

Calc. for $C_6H_5NClI.HCl$: 10.90. Found: 10.77, 10.64.

The acetanilide from the amine and acetic anhydride melts at 199°.

Calc. for C_8H_7ONBrI: N, 4.11. Found: 4.30, 4.02.

In the case of the *m*-chloroaniline, as is noted later, the iodine atom entered the 4-position. It is very probable that the same reaction occurred here, but the exact proof must be deferred until later.

The Introduction of Iodine into the Chloroanilines.

Preparation of 4-Chloroiodoaniline.—These react under the usual conditions and on distilling the product with steam, an oil comes over which slowly solidifies. The compound, which melts at 46°, can be purified by dissolving in gasoline and cooling with ice, or it can be crystallized from hot water, in which it is slightly soluble.

Calc. for $C_6H_5ClINH_2$: N, 5.52; Cl, 14.00; I, 50.07. Found: N, 5.63; Cl, 14.01; I, 50.13.

The analysis and reactions indicate that it is a 4-chloroiodoaniline and from analogy to the 4-bromo-2-iodoaniline, the iodine has doubtless entered the 2-position, although that point will be proved definitely later.

Derivatives of 4-Chloroiodoaniline.—The hydrochloride melts with decomposition at 202°.

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Calc. for $C_6H_5NClI.HCl$: HCl, 12.58. Found: 12.51, 12.60.

4-Chloroiodoacetanilide, from acetic anhydride and the aniline gives white crystals from alcohol, melting at 150°.

Calc. for C_8H_7ONClI: N, 4.74. Found: 4.75, 4.86.

The benzanilide melts at 145° and can be purified by crystallization from gasoline or alcohol.

Calc. for $C_{13}H_9ONClI$: Cl, 9.93; I, 35.52. Found: Cl, 9.98, 9.94; I, 35.70, 35.22.

In one experiment, using only molar quantities of *p*-chloroaniline and iodine, there was obtained as the main product *p*-chlorodiiodoaniline. The black solid formed was purified by recrystallization from alcohol, from which it separated in white needles, melting at 129°.

Calc. for $C_6H_4NClI_2$: N, 3.69. Found: 3.63, 3.80.

The introduction of 3 halogen atoms has decreased the reactivity of the compound. It failed to form a hydrochloride in benzene solution, nor did it give an acetyl derivative on boiling with acetic anhydride and sodium acetate.

When heated with benzoyl chloride, the benzanilide was obtained. This, after purification from alcohol, melted at 205°.

Calc. for $C_{13}H_9ONClI_2$: N, 2.97. Found: 3.09, 3.27.

Preparation of 2-Chloro-4-iodoaniline.—A molar mixture of *o*-chloroaniline and iodine, together with calcium carbonate, ether and water was heated and the reaction product distilled with steam. A brown oil came over which slowly solidified. It was purified by solution in alcohol and boiling with animal charcoal. Water precipitated from the alcohol solution white crystals which melted at 73°.

Calc. for $C_6H_5ClINH_2$: N, 5.52. Found: 5.53, 5.64.

The compound is identical with a 4-iodochloroaniline (m. p. 73°) obtained by Werner and Caldwell.[1] Starting with *p*-iodoacetanilide, they made the iodidechloride $CH_3CONHC_6H_4ICl_2$. This, on heating, gave the 4-iodochloroacetanilide (m. p. 144°), which on hydrolysis yielded the 4-iodochloroaniline (m. p. 73°). They obtained a picrate (m. p. 132°) and with phenyl isothiocyanate, the thiourea (m. p. 158°). The aniline (m. p. 73°) which we obtained gave also an acetyl, picrate, and a mustard oil derivative with the above melting points, the formula of each compound being confirmed by analysis. Its constitution as a 2-chloro-4-iodoaniline is therefore established, since in one case the starting point was 2-chloro- and in the other 4-iodoaniline.

Derivatives of 2-Chloro-4-iodoaniline.—The hydrochloride melts with decomposition at 190°.

Calc. for $C_6H_5NClI.HCl$: HCl, 12.58. Found: 12.50, 12.44.

[1] *J. Chem. Soc.*, 91, 246 (1907).

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The benzanilide is slightly soluble in cold alcohol, and melts at 165°.

Calc. for $C_{13}H_9ONClI$: N, 3.92. Found: 3.99, 4.11.

The phenyl urea $C_6H_3ClINHCONH_2$ can be crystallized from alcohol, and has a melting point of 175°.

Calc. for $C_7H_6ON_2ClI$: Cl, 11.97; I, 42.83. Found: Cl, 11.88, 12.05; I, 42.53, 43.15.

Preparation and Proof of Constitution of 3-Chloro-4-iodoaniline.—*m*-Chloroaniline was allowed to react with iodine in the usual manner. The steam distillate on standing deposited crystals which were filtered off, dissolved in alcohol and decolorized with animal charcoal. The alcoholic solution on diluting with ice water deposited the pure 3-chloro-4-iodoaniline, which melted at 65°. The yield was poor.

Calc. for C_6H_5NClI: N, 5.52. Found: 5.57, 5.49.

It has been shown that in the iodination of the 2-chloroaniline, the iodine entered the 4-position. If the same 4-position is occupied when 3-chloroaniline is treated with iodine, then on replacing the amino group by iodine, both chloroiodoanilines would give the same 1,4-diiodo-2-chlorobenzene. Experiment proved this to be the case.

2-Chloro-4-iodoaniline was diazotized and treated at 0° with a solution of potassium iodide. On standing a dark red oil separated. The contents of the flask were warmed and distilled with steam. The dark oil which came over solidified on standing. This, after boiling in alcohol with animal charcoal, gave white crystals melting at 51°. The analysis corresponded to a diiodochlorobenzene.

Calc. for $C_6H_3ClI_2$: Cl, 9.74; I, 69.68. Found: Cl, 9.68, 8.74; I, 69.55, 70.18.

When the supposed 3-chloro-4-iodoaniline was diazotized in the same manner, it gave a diiodochlorobenzene, melting at 51° and identical in every way with the known 1,4-diiodo-2-chlorobenzene.

Derivatives of 3-Chloro-4-iodoaniline.—The hydrochloride separates in the form of white crystals, melting with decomposition at 180°.

Calc. for $C_6H_5NClI.HCl$: HCl, 12.58. Found: 12.59, 12.47.

Acetic anhydride readily gives the 3-chloro-4-iodoacetanilide, which crystallizes from alcohol in white needles, with a melting point of 170°.

Calc. for $CH_3CONHC_6H_3ClI$: N, 4.72. Found: 4.73, 4.82.

The benzanilide melts at 144°.

Calc. for $C_{13}H_9ONClI$: N, 3.92. Found: 3.88, 3.78.

Preparation of 2,4-Dichloroiodoaniline.—While iodine and aniline react readily, giving the 2,4,6-triiodoaniline, the introduction of iodine into the 2,4-dichloroaniline occurs only with difficulty. Ten hours' heating of the 2 substances gave only a small yield of white crystalline product, slowly volatile with steam, which melted at 85°. Analysis showed this to be the 2,4-dichloro-6?-iodoaniline.

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Calc. for $C_6H_2Cl_2INH_2$: N, 4.83; Cl, 24.65; I, 4.09. Found: N, 4.76; Cl, 24.65; I, 43.98.

The compound, when dissolved in benzene and treated with hydrogen chloride, gave an impure hydrochloride, melting at 180°. There was found on analysis only 8.25% HCl instead of the required 11.25%. Even this amount decreased rapidly on standing.

The Action of Iodine on Non-halogenated Aromatic Amines.—The investigations on the direct introduction of iodine in the foregoing fashion have dealt with aniline, the halogen anilines or the toluidines. In the majority of cases it has been found that the reaction proceeds fairly smoothly, good yields being obtained. When, however, the hydrogen of the ring is replaced with 2 or 3 methyl groups or with a methoxy, ethoxy or acetamino grouping, the yield of the simple iodine derivative may be very much lessened or there may be formed only resinous, iodine-containing condensation products. Under like conditions the mono- and dimethylanilines tend to give the same complex resins.

Pseudocumidine reacts with iodine, giving a large amount of resinous material and a small yield of 2-iodo-3,4,6-trimethylaniline, melting at 93°.

Calc. for $C_9H_{12}NI$: N, 5.36. Found: 5.44, 5.46.

This had been previously prepared by Kirschbaum by the action of iodine monochloride on the cumidine. The hydrochloride melts at 192–3°. In like manner he obtained 6-iodo-2,4-dimethylaniline[1] (m. p. 65°), also formed from iodine and as *m*-xylidine.

Calc. for $C_8H_{10}NI$: N, 5.67. Found: 5.63, 5.52.

o-Anisidine and iodine react, yielding a product slowly volatile with steam, which, after crystallization from dilute alcohol, melted at 49°. The analytical figures and reactions indicate that it is a 2-methoxy-4?-iodoaniline.

Calc. for C_7H_8ONI: N, 5.62; I, 51.00. Found: N, 5.29; I, 50.76.

The hydrochloride melts at 180°.

Calc. for C_7H_8ONI: HCl, 12.78. Found: 12.88.

The iodo-2-methoxyacetanilide, after recrystallization from alcohol, had a melting point of 176°.

Calc. for $C_9H_{10}O_2NI$: N, 4.81; I, 43.69. Found: N, 4.88; I, 43.79.

When *p*-anisidine was heated with iodine, the only product obtained was a black, waxy, resinous substance, somewhat soluble in alcohol, acetone and benzene, and readily soluble in pyridine. It was found impossible to purify it satisfactorily. Analysis showed that it contained iodine, and it would seem probable that it was a condensation product of two or more moles of an iodo-*p*-anisidine.

[1] *Ber.*, **28**, 2799, 2809 (1895).

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p-Acetphenylenediamine behaved in a similar manner. The reaction product consisted of a black iodine-containing solid melting between 240–50° and only slightly soluble in the usual organic solvents.

The Determination of Halogens in Organic Compounds.

The halogen determinations in the preceding paper were made by a liquid ammonia process which has been found to give very good results in this laboratory and to be much simpler than the usual methods. Some years ago Dr. H. P. Cady noted the fact that when sodium was added to an organic halogen derivative in liquid ammonia, the halogen was removed quantitatively. Enough experimental work was carried on to indicate that the method was a practical one. Somewhat later it was developed more fully in the organic laboratory and has been used successfully for several years. After this had been done it was found that the same procedure had been devised by E. Chablay.[1]

The following method, though essentially the same, is somewhat more convenient than that of Chablay. A small quantity of the substance (usually less than 0.1 g. in the case of iodine compounds) is placed in a Dewar bulb and about 30 cc. of liquid ammonia added. When the material is in solution, although this is not essential if it is finely divided, a small piece of sodium is added. An excess is used, which is indicated by the blue color of the solution. The material is stirred and allowed to stand until all the ammonia has evaporated. The excess of sodium can be taken up in the ammonia solution with solid ammonium nitrate, or a little alcohol can be added to the residue. This is not necessary, however, unless a large excess of sodium has been used. The residue, after the evaporation of the ammonia, is dissolved in water, acidified with nitric acid, an excess of 0.1 *N* or 0.025 *N* silver nitrate added, filtered and the filtrate titrated with standard ammonium thiocyanate solution, using ferric alum as an indicator.

The process can be recommended as the shortest and most simple method for halogen determinations in organic compounds. It may be of interest to note that calcium, which is also soluble in liquid ammonia, has been used with success in the determination of chlorine in 4-chloroaniline.

Summary.

Experimental work has been carried out along the following lines:

(1) The action of iodine on chloro- and bromoanilines.

(2) The action of iodine on cumidine, xylidine, anisidine and acetphenylenediamine.

(3) A method for the determination of halogens in organic compounds.

[1] *Ann. chim.*, [9] 1, 516 (1914).

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF CORNELL UNIVERSITY.]

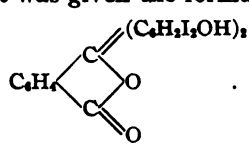
TETRAIODOPHENOLPHTHALEIN AND TETRAIODOPHENOL-TETRACHLOROPHTHALEIN AND SOME OF THEIR DERIVATIVES.

BY W. R. ORNDORFF AND S. A. MAHOOD.

Received January 19, 1918.

Historical.

Tetraiodophenolphthalein was first prepared by Classen and Löb.[1] Six g. of phenolphthalein was dissolved in 100 cc. of water containing 8 g. of sodium hydroxide and to this was added at room temperature a solution containing 20 g. of iodine (8 atoms[2]) and 20 g. of potassium iodide in 100 cc. of water. The color of the solution gradually changed from red to blue and was a yellowish brown after all the iodine had been added. On acidification a porridge-like mass was precipitated which, after washing, was purified by again dissolving in caustic soda and precipitating with acid. The precipitate was then suspended in water and steam passed into the mixture. The product obtained in this way was an amorphous, almost white, powder which decomposed without melting at about 220°, giving off iodine. It dissolves easily in alkalies, with which it may be boiled without undergoing any change. It is insoluble in water and acids, difficultly soluble in alcohol, but somewhat more easily soluble in glacial acetic acid, chloroform and ether. Analysis confirmed the formula $C_{20}H_{10}O_4I_4$. As it is quite analogous in its conduct to Baeyer's tetrabromophenolphthalein[3] it was given the formula



The compound was obtained in the form of pale yellow granular crystals by dissolving the amorphous product in alcoholic sodium hydroxide solution and precipitating at the boiling point with alcoholic hydrochloric acid.

Just as Baeyer[4] found in the case of phenolphthalein that the red color of the sodium salt disappears on the addition of a large excess of alkali with a breaking of the anhydride condition, so the blue sodium salt of tetraiodophenolphthalein is converted into the colorless salt of the corresponding carbinolcarboxylic acid by treatment with alkali.

When a strong alkaline solution of tetraiodophenolphthalein was cooled

[1] *Ber.*, **28**, 1603 (1895).

[2] This is 4.5% more than the calculated amount of iodine (8 atoms).

[3] *Ann.*, **202**, 68 (1880).

[4] *Loc. cit.*

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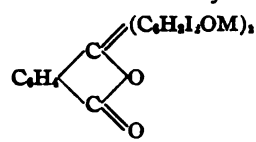
to —5° and hydrochloric acid also cooled below 0° added, with continual cooling, a yellowish brown precipitate separated out. When dried on a porous plate, taken up in chloroform, precipitated with ligroin and then dried *in vacuo* at ordinary temperatures, analyses showed it to be the tetraiodophenolphthaleincarbinolcarboxylic acid differing from the phthalein only by one molecule of water. Most characteristic is the difference in solubility in chloroform and ether in which the acid dissolves very readily. It dissolves in caustic soda with a blue color and gives the above-described tetraiodophenolphthalein on precipitating it without cooling with acids. It may also be converted into the last named compound by heating it to about 100°.

Iodination of phenolphthalein was also carried out in solutions of ammonium hydroxide, barium hydroxide, alcohol, borax and by the electrolysis of an alkaline solution containing potassium iodide. The tetraiodo product resulted in all cases.

The authors state that the alkali salts of tetraiodophenolphthalein were obtained by evaporation of the neutral solutions of the phthalein in the alkalies. The sodium and potassium salts form pure blue prisms easily soluble in water and alcohol. They have the following structure:



The salts of various other metals were obtained by treating solutions of the sodium salt with solutions of metallic salts.

Patents were taken out by Classen covering the foregoing methods for the preparation of iodine derivatives of phenolphthalein.[1]

In the first patent[2] the method for iodinating in alkaline solution is modified by increasing the strength of alkali in which the phenolphthalein is dissolved from 2 *N* to 10 *N*. The amount of water in which the potassium iodide and iodine are dissolved is also changed so that the concentration of alkali in the reaction mixture is twice that used in the above method of preparation. The patent states that if the reaction mixture is kept below 20° and acidified, the carbinolcarboxylic acid is precipitated. It is purified by dissolving the undried product in chloroform and precipitating it with ligroin. If the reaction mixture is heated for some time on a steam bath and then acidified, tetraiodophenolphthalein is precipitated.

A patent was also taken out by Kalle & Company for the preparation

[1] D. R. P. 85,930, Frdl., 4, 1090; D. R. P. 87,785, *Ibid.*, 4, 1091; D. R. P. 88,390, *Ibid.*, 4, 1093; D. R. P. 86,069, *Ibid.*, 4, 1094.

[2] D. R. P. 85,930, Frdl., 4, 1090.

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of tetraiodophenolphthalein by the action of iodine chloride on phenolphthalein in hydrochloric acid solution or glacial acetic acid.[1]

This investigation was undertaken for the purpose of studying the effect on the chemical conduct and general properties of phenolphthalein and phenoltetrachlorophthalein of the introduction of iodine into the phenol part of the phthalein molecule, and to further study the relation of constitution to color in this class of compounds.

A review of the investigations carried out to determine the relationship between color and constitution of the phthaleins and their salts will be found in papers previously published from this laboratory.[2]

Experimental.

In this investigation the iodine determinations were made either by the lime method described by Delbridge[3] or by the permanganate oxidation method of Seeker and Mathewson.[4] Both methods were modified somewhat.

In the lime method some calcium iodate is formed[5] which must be reduced before adding the silver nitrate, while the temperature must be kept down during the acidification with nitric acid in order to prevent the loss of iodine by the oxidation of the hydriodic acid liberated. After heating the substance with lime in the usual way, the contents of the tube was emptied into a flask containing 100 cc. of water, 5 cc. of a saturated solution of sulfur dioxide was added and the flask shaken. The mixture was then cooled to about 15° and 6 *N* nitric acid added gradually in portions of 10 to 25 cc. The flask was shaken during the addition of the acid and cooled so that no rise in temperature occurred. About 125 cc. of the acid was required to dissolve the lime completely. When solution was complete an *excess* of 0.1 *N* silver nitrate was added, the carbon, insoluble material and silver iodide filtered off, and the silver nitrate in the filtrate titrated with ammonium thiocyanate, using ferric ammonium sulfate as indicator.

In the simultaneous determination of iodine and chlorine the same procedure was followed except that the carbon and insoluble material were filtered off before the addition of silver nitrate and the precipitated halides were collected on weighed Gooch crucibles and their weight determined after drying at 145°. From the weight of the silver halides and the volume of 0.1 *N* silver nitrate required to precipitate them,

[1] D. R. P. 143,596, Frdl., 7, 631.

[2] *Am. Chem. J.*, **42**, 183 (1909); THIS JOURNAL, **36**, 680 (1914); *Ibid.*, **37**, 1201 (1915).

[3] *Am. Chem. J.*, **41**, 397 (1909).

[4] *Chem. News*, **103**, 61 (1911).

[5] Meyer, "Analyse und Konstitutionsermittelung Organischer Verbindungen," 1909, p. 206.

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the percentages of iodine and chlorine in the original compound can be calculated by means of the following formulas:[1]

$$\text{Percentage of iodine} = 138.77B - 1.9892C/A$$
$$\text{Percentage of chlorine} = 0.9103C - 38.769B/A$$

in which A = weight of substance taken.
B = weight of silver halides.
C = the volume in cc. of 0.1 N silver nitrate solution required to precipitate the silver halides.

As a check upon this indirect method of analysis, the silver halides were heated to just below the fusion point and treated with dry chlorine. This replaced all of the iodine in the silver iodide by chlorine. From the loss in weight and the weight of the silver halides, the halogen content of the original compound can be calculated from the formulas

$$\text{Percentage of iodine} = 138.77D/A.$$
$$\text{Percentage of chlorine} = 24.738B - 63.511D/A.$$

in which A = weight of substance taken.
B = weight of silver halides.
D = loss in weight of the silver halides on treatment with chlorine.

The permanganate oxidation method is especially applicable in the case of compounds containing iodine and chlorine or bromine, but it may be employed to advantage where only iodine is present, for it is fully as accurate and quite as rapid as the lime method where the acidification at a low temperature requires considerable time. If the permanganate oxidation method is modified by titrating the excess of silver nitrate instead of weighing the silver iodide, the time required is considerably shorter than in the lime method. The method of Seeker and Mathewson was followed except that an excess of 0.1 N silver nitrate was added and the silver iodide filtered off on a hardened filter and washed thoroughly with 1% nitric acid. The filtrate was treated with 10 cc. of conc. nitric acid, and the silver nitrate titrated as in the lime method.

That the two methods as modified give concordant results is shown by the following analyses:

		Substance. Gram.	0.1 N silver nitrate. Cc.	Iodine. %.
Lime	I	0.3675	17.68	61.06
Method	II	0.4026	19.42	61.22
Oxidation	III	0.4564	21.94	61.01
Method	IV	0.4096	19.70	61.04

Similar results were obtained throughout this investigation and good agreement with the theory was obtained by both methods when pure compounds were analyzed.

The results for iodine by the oxidation method were occasionally found to run a little higher when the silver iodide was weighed than when the excess of silver nitrate was titrated. This was found to be due to small

[1] *Am. Chem. J.*, 41, 380 (1909); THIS JOURNAL, 36, 702 (1914).

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amounts of suspended material in the solution after treatment with sulfur dioxide. By filtering the solution through a hardened filter before adding the silver nitrate, results were obtained which were in complete accord, consequently when the titrations were checked by weighing the silver iodide this additional modification was made in the oxidation method.

Tetraiodophenolphthalein.—This compound was prepared by treating phenolphthalein in alkaline solution with a little more than the calculated amount of iodine. It was found that the method described in the patent[1] gave small amounts of a tar-like material which colored the phthalein yellowish brown and rendered it exceedingly difficult to purify. This material was formed in much smaller amounts when the iodination was carried out in more dilute alkaline solution, hence the method described in the paper[2] of Classen and Löb was followed with some modifications.

The phenolphthalein used was a pure white product which darkened at 250° and melted at 254°. It dissolved completely in 2% alkali and hence was free from fluoran. The iodine used was the resublimed material.

The procedure in iodinating the phthalein was as follows: Thirty g. of phenolphthalein was dissolved in 500 cc. of 2 *N* sodium hydroxide. This solution was stirred mechanically and to it was added, in the course of half an hour, a solution containing 100 g. of iodine and 120 g. of potassium iodide in 500 cc. of water. The color darkened perceptibly and became a reddish blue after all of the iodine had been added. The reaction mixture was stirred for 8 hours. No apparent change in color took place in this time.

Acidification with strong hydrochloric acid as directed by Classen and Löb not only precipitates the phthalein but liberates some of the combined iodine in the inorganic salts, which gives the phthalein a deep brown color difficult to remove. To minimize this liberation of iodine, the reaction mixture was carefully neutralized with 2 *N* acetic acid while being mechanically stirred. A grayish white precipitate settled out which was readily filtered off with the aid of suction. The filtrate had a slight yellow color. It gave no precipitate with hydrochloric acid but darkened in color, due to the liberation of iodine. The precipitate was dissolved in 2% alkali and the solution acidified with acetic acid, an excess of the acid being avoided on account of the solubility of the phthalein in acetic acid. The precipitate when filtered off had a pale yellow color. The filtrate contained some free iodine. The phthalein was again dissolved in 2% alkali, the solution strongly acidified with hydrochloric acid and steam passed through it to coagulate the precipitate. The product thus obtained, when washed free from chlorides and air-dried had a slight tinge of yellow.

[1] D. R. P. 85,930, Frdl., **4**, 1090.

[2] *Ber.*, **28**, 1603 (1895).

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Yield, 87% of the theoretical calculated from the amount of phenolphthalein used.

The phthalein is difficultly soluble in methyl alcohol, ethyl alcohol, ether, chloroform, acetone, benzene, ethyl acetate and nitrobenzene, but readily soluble in pyridine. Acetone and a mixture of acetone and absolute ethyl alcohol were found to be the best solvents for use in purifying the phthalein although large volumes of these solvents had to be used on account of its slight solubility. By crystallization from acetone and then from acetone-ethyl alcohol, a perfectly colorless product was obtained in the form of microscopic needles. It decomposes at 270–272°[1] with the evolution of iodine and becomes brown. At 288–290° it becomes viscous, and changes to a brown liquid at 307–308°. The phthalein lost no weight in an electrically heated tube[2] at 150°. The air-dried sample was analyzed for iodine by the lime method.

Subst., (I) 0.4414, (II) 0.4113; cc. 0.1 *N* $AgNO_3$, (I) 21.48, (II) 19.99.
Calc. for $C_{20}H_{10}I_4O_4$: I, 61.77. Found: (I) 61.76, (II) 61.69.

The phthalein dissolves in alkalies with a reddish blue color which rapidly fades on standing and finally the solution becomes colorless. This tendency is more marked than in the case of phenolphthalein. In thin layers the color of the alkaline solution is blue. The compound is stable in solid form but its acetone solution becomes colored yellow on long standing, probably due to the liberation of iodine. The alkaline solution is less sensitive to carbon dioxide than that of phenolphthalein.

An attempt was made to prepare the carbinolcarboxylic acid by the method described by Classen and Löb. Five g. of the pure tetraiodophenolphthalein was dissolved in 50 cc. of 6 *N* sodium hydroxide. The solution had a light yellowish green color. It was diluted to 1.5 *N* and cooled to —12°. It then had only a faint yellow color. This alkaline solution was added to an excess of 6 *N* hydrochloric acid cooled to —7°. The temperature of the reaction mixture was not allowed to go above —2°. A *white* flocculent precipitate came down which readily settled. The supernatant liquid was decanted off, water added, the precipitate allowed to settle and the supernatant liquid again poured off. The precipitate was washed in this way until the wash water gave no test for chlorides. The precipitate was then filtered off and dried to constant weight *in vacuo*. A portion was then further dried by heating.

Subst., 0.4546: loss at 110°, 0.0029; loss at 160°, 0.0033.

Calc. for $C_{20}H_{10}I_4O_4.H_2O$: H_2O, 2.14. Found: H_2O at 110°, 0.64; total loss at 160°, 0.73.

[1] Melting points and decomposition temperatures are uncorrected and were made in an electrically heated Thiele apparatus.

[2] THIS JOURNAL, 32, 635 (1910); *Am. Chem. J.*, 48, 477 (1912).

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The sample dried at 160° was analyzed by the permanganate oxidation method.

Subst., (I) 0.2062, (II) 0.2366; cc. 0.1 *N* $AgNO_3$, (I) 10.02, (II) 11.48.
Calc. for $C_{20}H_{10}I_4O_4$: I, 61.77. Found: (I) 61.68, (II) 61.58.

These results show that the product precipitated at low temperatures is tetraiodophenolphthalein and not the carbinolcarboxylic acid as stated by Classen and Löb. It seems highly probable that their product was impure since they describe it as having a yellowish brown color while the product which we obtained starting with the pure phthalein is absolutely colorless.

Tetraiodophenolphthalein Diacetate.—Fifteen g. of the phthalein was boiled with 10 times its weight of redistilled acetic anhydride. The phthalein went into solution soon after the boiling began. The light yellow solution was boiled for one and a quarter hours, filtered, concentrated and allowed to cool when colorless rectangular plates separated out. These were filtered off, the filtrate further concentrated and a second crop of crystals obtained. Yield, 83%. The diacetate is quite soluble in benzene, ethyl acetate and chloroform, soluble in ether and somewhat soluble in methyl and in ethyl alcohol. The product crystallized from benzene melted at 245°. Recrystallization from benzene did not change the melting point. The product from benzene crystallized from ethyl acetate in needles melting at 246°. A sample dried at 150° gave the following results on analysis by the lime method:

Subst., (I) 0.4418, (II) 0.3695; cc. 0.1 *N* $AgNO_3$, (I) 19.62, (II) 16.32.
Calc. for $C_{20}H_8I_4O_4(COCH_3)_2$: I, 56.04. Found: (I) 56.36, (II) 56.06.

The diacetate is not changed by cold aqueous alkali but gives a blue color when warmed with it. When treated with an excess of alcoholic caustic potash in the cold and shaken for some time it dissolves completely, giving practically no color to the solution. Water and acid were added to the alcoholic alkaline solution and the precipitated phthalein filtered off, washed thoroughly, dried at 150°, and analyzed by the lime method.

Subst., 0.3325; cc. 0.1 *N* $AgNO_3$, 16.16.
Calc. for $C_{20}H_{10}I_4O_4$: I, 61.77. Found: 61.69.

Tetraiodophenolphthalein Dibenzoate.—Twenty g. of the phthalein was dissolved in 200 cc. of water containing 13.6 g. of potassium hydroxide. Twice the calculated amount of benzoyl chloride necessary to react with the phthalein was added and the mixture shaken in a 500 cc. wide-mouth glass-stoppered bottle. More alkali and benzoyl chloride were added from time to time until the alkaline solution no longer had a blue color. The reaction mixture had a faint odor of benzoyl chloride and was alkaline. The reddish powder which formed was shaken with soda solution, filtered and washed thoroughly. Yield, 72%. The di-

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benzoate is readily soluble in benzene, ethyl acetate and acetone, difficultly soluble in methyl and in ethyl alcohol and insoluble in ether. Crystallized from a mixture of ethyl alcohol and benzene it melted at 298°. When crystallized from benzene alone it was obtained in colorless rectangular plates melting at 298°. A portion of the dibenzoate dried at 160° was analyzed by the lime method.

Subst., (I) 0.2621, (II) 0.2904; cc. 0.1 *N* $AgNO_3$, (I) 10.20, (II) 11.21.
Calc. for $C_{20}H_8I_4O_4(COC_6H_5)_2$: I, 49.29. Found: (I) 49.39, (II) 48.99.

The dibenzoate is unaffected by aqueous alkalies but is quite readily saponified by boiling alcoholic alkalies.

Tetraiodophenolphthaleinoxime.—In preparing this compound the method of Friedlander was used.[1] Four g. of pure tetraiodophenolphthalein was dissolved in 25 cc. of water containing 1.7 g. of potassium hydroxide. Eight-tenths g. of pure hydroxylamine hydrochloride was added to the hot alkaline phthalein solution and the mixture heated at 95° on a water bath for a quarter of an hour. The color changed from reddish violet to pale green. 2 *N* acetic acid was then added in excess to the hot solution, giving a yellow flocculent precipitate which was readily filtered off. The precipitate was washed with hot water and air dried, yield practically quantitative. Recrystallized from benzene, the oxime came down in almost colorless, diamond-shaped glistening plates which in the aggregate appeared light brown. These crystals decomposed (reddish color) at 135° and liquefied at 170°. Iodine determinations by the permanganate oxidation method on a sample of the oxime dried at 85° gave the following results:

Subst., (I) 0.1909, (II) 0.2564; cc. 0.1 *N* $AgNO_3$, (I) 9.14, (II) 12.31.
Calc. for $C_{20}H_{11}I_4O_4N$: I, 60.67. Found: (I) 60.77, (II) 60.94.

Nitrogen determinations were made on the oxime, dried at 85°, by the Kjeldahl method after reduction with zinc dust.

Subst., (I) 0.1537, (II) 0.1389; cc. 0.1 *N* HCl, (I) 1.73, (II) 1.76.
Calc. for $C_{20}H_{11}I_4O_4N$: N, 1.67. Found: (I) 1.58, (II) 1.78.

The oxime dissolved in alkalies with a yellow color. It is readily soluble in absolute ethyl alcohol, benzene, acetone and ether; quite soluble in methyl alcohol; insoluble in petroleum ether.

Action of Dry Ammonia on Tetraiodophenolphthalein.—Gaseous ammonia dried by passing it through soda lime and then through a tube containing sodium wire was allowed to act on a weighed amount of tetraiodophenolphthalein. The phthalein became bright blue in 15 minutes and a weighing showed it had taken up approximately 2 molecules of ammonia. The weight of the salt became constant in an hour and a quarter.

[1] *Ber.*, **26**, 173 (1893).

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Subst., (I) 0.3794, (II) 0.2813; gain, (I) 0.0319, (II) 0.0235.
Calc. for $C_{20}H_{10}I_4O_4.4NH_3$: NH_3, 7.67. Found: (I) 7.76, (II) 7.71.

In a current of dry air at room temperature 2 molecules of the ammonia are lost in half an hour. The remaining two molecules are lost very slowly. Not all of the ammonia was lost in dry air at the end of 36 hours. It was all given up, however, if the salt was heated to 60° for 4 hours or allowed to stand in a desiccator over calcium chloride for several weeks.

Compound of Tetraiodophenolphthalein with Pyridine.—In attempting to find a suitable solvent from which to crystallize the phthalein, it was found that it is so excessively soluble in pyridine that it will not crystallize out. Four times its volume of absolute ethyl alcohol was added to the pyridine solution and the mixture allowed to stand for some time when a voluminous mass of hair-like needles separated out, which, when filtered off, had a faint yellow color. The crystals were washed thoroughly with absolute alcohol and allowed to dry in the air for half an hour. The material was then bottled and a sample analyzed by the permanganate oxidation method.

Subst., (I) 0.3667, (II) 0.4163; cc. 0.1 *N* $AgNO_3$, (I) 13.92, (II) 15.85.
Calc. for $C_{20}H_{10}I_4O_4.3C_5H_5N$: I, 47.94. Found: (I) 48.18, (II) 48.32.

After standing in a glass-stoppered bottle for two days a portion of the compound was dried to constant weight at 130–140°.

Subst., 0.2336; loss, 0.0413.
Calc. for $C_{20}H_{10}I_4O_4.3C_5H_5N$: C_5H_5N, 22.40.
Calc. for $C_{20}H_{10}I_4O_4.2C_5H_5N$: C_5H_5N, 16.14. Found: 17.68.

No further loss occurred when the sample was heated to 200°, but the sample took on a brownish color at 160°. Analysis of the sample dried at 130–140° showed it had lost all of the pyridine.

Subst., 0.1916; cc. 0.1 *N* $AgNO_3$, 9.29.
Calc. for $C_{20}H_{10}I_4O_4$: I, 61.77. Found: 61.54.

Monopotassium Salt of Tetraiodophenolphthaleincarbinolcarboxylic Acid.—To obtain this salt 5 g. of the pure phthalein was suspended in 100 cc. of 95% alcohol. To this was added 1.5 g. of potassium acetate in 100 cc. of 95% alcohol. The mixture was boiled in a flask connected with a return condenser for one hour Not all of the material went into solution, so more alcohol was added from time to time and the boiling continued until solution was complete. The solution had a faint blue color. It was concentrated and allowed to stand when crystals with a very faint green tint separated out. These were filtered off and washed with 95% alcohol. When dry they were practically colorless. After standing in a glass-stoppered bottle for several months, samples of the salt were heated to constant weight at 160–170° in a current of dry air free from carbon dioxide. Water collected on the cool part of the tube, and

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the salt became green at 140–145°. As the temperature increased the color deepened. Heated above 170° the salt decomposed.

Subst., (I) 0.2806, (II) 0.1900; loss in weight, (I) 0.0077, (II) 0.0053.
Calc. for $C_{20}H_9I_4O_4K.1.5H_2O$: H_2O, 3.04. Found: (I) 2.74, (II) 2.79.

Samples of the undried salt were analyzed for iodine by the oxidation method.

Subst., (I) 0.2351, (II) 0.2127; cc. 0.1 *N* $AgNO_3$, (I) 10.56, (II) 9.53.
Calc. for $C_{20}H_9I_4O_4K.1.5H_2O$: I, 57.24. Found: (I) 57.01, (II) 56.87.

Potassium determinations were made on portions of the undried material by fuming down with sulfuric acid.

Subst., (I) 0.2148, (II) 0.2284; K_2SO_4, (I) 0.0207, (II) 0.0218.
Calc. for $C_{20}H_9I_4O_4K.1.5H_2O$: K, 4.40. Found: (I) 4.33, (II) 4.28.

This colorless compound is therefore the salt of tetraiodophenolphthaleincarbinolcarboxylic acid. When heated it loses water and changes to the green monopotassium salt of the phthalein. It is difficultly soluble in water, but gradually goes into solution in boiling water with the production of a blue color. When a large amount of water is added and the solution boiled the salt is hydrolyzed and the free phthalein is precipitated.[1]

Disodium Salt of Tetraiodophenolphthaleincarbinolcarboxylic Acid.—In the preparation of this compound 0.4270 g. of sodium was dissolved in 100 cc. of absolute ethyl alcohol and 7.6281 g. of pure tetraiodophenolphthalein added. On warming the mixture the phthalein dissolved completely, giving the solution a reddish blue color in thick layers and a blue color in thin layers. The solution was concentrated to one-half its volume and allowed to stand. Large clusters of pale green crystals formed. These were filtered off and washed with absolute alcohol. When exposed to the air the crystals began to effloresce. Some of the crystals were ground in a mortar, the pulverized material transferred to a platinum boat, weighed and allowed to stand in a desiccator over calcium chloride and sodium hydroxide. On grinding the product became a white powder which immediately assumed a faint blue color. Standing in the desiccator for 12 hours, the salt lost weight and the color became more pronounced. On heating in a current of dry air free from carbon dioxide to 110°, further loss in weight occurred and the color became a deep blue. Moisture collected on the cool part of the tube and alcohol was given off as was shown by passing the escaping vapors into water, which gave a test for alcohol. The salt was dried to constant weight at 150–160°.

Subst., 0.2553; loss in weight, 0.0567.
Calc. for $C_{20}H_8I_4O_4Na_2.5C_2H_6O.H_2O$: 22.30. Found: 22.21.

[1] THIS JOURNAL, 34, 1424 (1912); *Ibid.*, 37, 1222 (1915).

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Sodium determinations were made on the dried product by fuming down with concentrated sulfuric acid.

Subst., (I) 0.2415, (II) 0.1403; Na_2SO_4, (I) 0.0394, (II) 0.0227.
Calc. for $C_{20}H_8I_4O_4Na_2$: Na, 5.31. Found: (I) 5.28, (II) 5.24.

A sample of the dried material was analyzed for iodine by the permanganate method.

Subst., 0.2907; cc. 0.1 *N* $AgNO_3$, 13.50.
Calc. for $C_{20}H_8I_4O_4Na_2$: I, 58.64. Found: 58.94.

A portion of the undried salt which had been ground to a powder, when exposed to the air for a short time, took on a deep blue color, which remained practically unchanged when this material was allowed to stand exposed to the air for several weeks.

The foregoing results show this compound to be the disodium salt of tetraiodophenolphthaleincarbinolcarboxylic acid which, when heated or allowed to stand exposed to the air, loses water and alcohol and forms the blue disodium salt of tetraiodophenolphthalein. Both salts dissolve in water with a blue color.

Tetraiodophenoltetrachlorophthalein.—This compound was prepared by iodinating phenoltetrachlorophthalein in alkaline solution. The phenoltetrachlorophthalein used for this purpose was made by the method of Orndorff and Black.[1] The tetrachlorophthalic acid used in the preparation of the latter compound was the commercial product purified by the method described by Delbridge.[2] The purity of the acid was checked by molecular-weight determinations made by titrating samples with standard sodium hydroxide.[3]

Subst., (I) 0.4252, (II) 0.3296; cc. 0.1 *N* NaOH, (I) 27.19, (II) 21.06.
Calc. for $C_6Cl_4(COOH)_2.0.5H_2O$: M. W., 312.9. Found: (I) 312.8, (II) 313.0.

The acid[4] was condensed with redistilled phenol which boiled at 180° and the phenoltetrachlorophthalein thus obtained, when purified and air-dried, gave the following results on analysis by the lime method:

Subst., (I) 0.2374, (II) 0.2806; cc. 0.1 *N* $AgNO_3$, (I) 20.70, (II) 24.53.
Calc. for $C_{20}H_{10}Cl_4O_4$: Cl, 31.10. Found: (I) 30.92, (II) 31.00.

The procedure in iodinating the phthalein was as follows: Twenty-five g. of the pure phenoltetrachlorophthalein was dissolved in 300 cc. of 2 *N* sodium hydroxide solution. This solution was mechanically stirred and to it was added, in the course of 20 minutes, an iodine solution containing 58.2 g. of iodine and 75 g. of potassium iodide in 300 cc. of water. The color changed rapidly from red to blue when all of the iodine had been added and the solution remained clear. The reaction

[1] *Am. Chem. J.*, 41, 349 (1909).
[2] *Ibid.*, 41, 414 (1909).
[3] *Ibid.*, 41, 399 (1909).
[4] THIS JOURNAL, 38, 2486 (1916).

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mixture was stirred for 9 hours at room temperature. 2 *N* acetic acid was then added to neutral reaction to litmus when a deep blue precipitate, a sodium salt of tetraiodophenoltetrachlorophthalein, separated out which was readily filtered off by the aid of suction. The filtrate had a yellowish brown color and gave no precipitate on being strongly acidified, but darkened, due to the liberation of iodine. The precipitate dissolved in water with a blue color. It was dissolved in water and 2% alkali, the solution stirred and 2 *N* acetic acid added to acid reaction. The phthalein came down as a yellowish green precipitate and was filtered off. The filtrate contained some free iodine. The precipitate was again dissolved in 2% alkali and this time acidified with conc. hydrochloric acid and steam passed through the mixture. The phthalein came out as a light brown material which became white as the mixture warmed up. It was washed by decantation, filtered off and air-dried. Yield, 85%.

Unlike tetraiodophenolphthalein, the tetraiodophenoltetrachlorophthalein is excessively soluble in acetone and absolute ethyl alcohol; readily soluble in benzene, ethyl acetate, methyl alcohol and chloroform and quite soluble in glacial acetic acid. Ethyl acetate proved the most suitable solvent for purifying the phthalein. On crystallization from this solvent 2 products were obtained, one as a crystalline powder which analysis showed to be a mixture of lower iodination products and the other in well-formed crystals which when recrystallized and analyzed proved to be the pure tetraiodophenoltetrachlorophthalein. It came out of ethyl acetate in thick diamond-shaped crystals. When heated in a melting-point tube it becomes blue at 202° due to reaction with the alkali of the glass, decomposes at 240–44° with the evolution of iodine and melts to a dark brown liquid at 250–55°. The crystals contain ethyl acetate which they lose on standing or when heated to 170°.

Subst., (I) 1.1819, (II) 0.5569, (III) 0.2438, (IV) 0.3255; loss in weight, (I) 0.0949, (II) 0.0437, (III) 0.0179, (IV) 0.0095.

Calc. for $C_{20}H_8I_4Cl_4O_4.C_4H_8O_2$: $C_4H_8O_2$, 8.41. Found: (I) 8.03, (II) 7.85, (III) 7.34, (IV) 2.92.

Determinations I and II were made on crystals which had been air-dried and then pulverized; Determination III was made on the same sample after standing for a month in a glass-stoppered bottle, and IV after standing 7 months.

In the analysis of compounds containing both chlorine and iodine by the permanganate oxidation method, the samples were treated a second time with 5 cc. of permanganate solution and 5 cc. of nitric acid and evaporated to dryness in order to insure the complete elimination of the chlorine. The following results were thus obtained on samples of the tetraiodophenoltetrachlorophthalein dried to constant weight at 170°:

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Subst., (I) 0.2496, (II) 0.2382; cc. 0.1 *N* $AgNO_3$, (I) 10.39, (II) 9.93.
Calc. for $C_{20}H_8I_4Cl_4O_4$: I, 52.90. Found: (I) 52.84, (II) 52.91.

To check the titration on these samples, the silver iodide was collected on weighed Gooch crucibles and dried to constant weight at 145°.

Subst., (I) 0.2496, (II) 0.2382; AgI, (I) 0.2440, (II) 0.2329.
Calc. for $C_{20}H_8I_4Cl_4O_4$: I, 52.90. Found: (I) 52.84, (II) 52.85.

Samples similarly dried were analyzed by the lime method.

	Substance. Gram.	Silver halides. Gram.	0.1 *N* silver nitrate. Cc.	% chlorine.	% iodine.
I.....	0.1872	0.2961	15.69	14.96	52.78
II.....	0.2435	0.3848	20.39	14.95	52.73
		Calc. for $C_{20}H_8I_4Cl_4O_4$:		14.78	52.90

The silver halides were treated with dry chlorine and the following results obtained:

	Substance. Gram.	Silver halides. Gram.	Decrease. Gram.	% chlorine.	% iodine.
I.....	0.1872	0.2961	0.0713	14.90	52.85
II.....	0.2435	0.3848	0.0930	14.84	53.00
		Calc. for $C_{20}H_8I_4Cl_4O_4$:		14.78	52.90

The phthalein dissolves in dilute alkalies with an almost pure blue color which does not fade appreciably on standing for several days. Strong alkalies precipitate the phthalein in the form of a blue-colored salt. The alkaline solution of tetraiodophenoltetrachlorophthalein is less sensitive to carbon dioxide than a similar solution of tetraiodophenolphthalein. The phthalein is stable in the solid form but its ethyl acetate solution turns brown on standing probably due to the liberation of some iodine.

Diacetate of Tetraiodophenoltetrachlorophthalein.—To prepare the diacetate 12 g. of the phthalein was boiled with 120 g. of acetic anhydried. The phthalein went into solution in 15 minutes after boiling began. The boiling was continued for one hour and after cooling the solution somewhat 108 g. of absolute ethyl alcohol was added. Fine needle-like crystals began to separate out which increased in quantity when the solution was allowed to stand. These were filtered off and the solution concentrated when more crystals came out. The diacetate was recrystallized from benzene from which it was obtained in the form of needles, which melted sharply at 262°. The product crystallized from benzene contains benzene of crystallization which it losses when dried at 200°.

Subst., (I) 0.4773, (II) 0.4610; loss in weight, (I) 0.0318, (II) 0.0382.
Calc. for $C_{20}H_4I_4Cl_4O_4(COCH_3)_2.C_6H_6$: C_6H_6, 6.96. Found: (I) 6.66, (II) 8.29.

Both samples were air-dried for one-half hour. Sample I had stood for 3 days in a glass-stoppered bottle.

Samples of the diacetates were analyzed by adding 5 cc. of 95% alcohol and 5 cc. of 10% sodium hydroxide solution and evaporating to dry-

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ness on the water bath, then adding 10 cc. of water and concentrating the solution to 5 cc. Iodine determinations were then made by the permanganate oxidation method.

Subst., (I) 0.2160, (II) 0.2275; cc. 0.1 N $AgNO_3$, (I) 8.26, (II) 8.74.
Calc. for $C_{20}H_4I_4Cl_4O_4(COCH_3)_2$: I, 48.64. Found: (I) 48.54, (II) 48.76.

The diacetate is unaffected by cold 2 N aqueous alkali but saponifies when boiled with this reagent. It is soluble in acetone, benzene and ethyl acetate, difficultly soluble in absolute ethyl alcohol.

Dibenzoate of Tetraiodophenoltetrachlorophthalein.—An attempt was made to prepare this compound by boiling 10 g. of the phthalein with 100 g. of benzoyl chloride. The phthalein went into solution quite readily, but when the solution began to boil iodine was liberated, showing that the phthalein was being decomposed. The Baumann-Schotten method was therefore used in preparing the dibenzoate.

Six g. of tetraiodophenoltetrachlorophthalein was dissolved in 240 cc. of $^1/_3$ N sodium hydroxide and 4 g. of benzoyl chloride added. The mixture was stirred and alkali and benzoyl chloride added from time to time until the color of the solution became somewhat lighter. The dibenzoate settled to the bottom of the container as yellow granular particles. It was filtered off, triturated with sodium carbonate solution, and again filtered off, washed, and air-dried. Yield, 82%.

The dibenzoate is not affected by cold aqueous sodium hydroxide but is slowly saponified when heated with it. It is quite readily saponified by hot alcoholic caustic soda. It is readily soluble in benzene, ethyl acetate, ether and chloroform, somewhat soluble in methyl and in ethyl alcohol and insoluble in petroleum ether. When recrystallized from methyl alcohol the dibenzoate was obtained in the form of white flakes containing no methyl alcohol of crystallization and melting to a colorless liquid at 205°. In the analysis by the permanganate oxidation method, samples of the dibenzoate were saponified by adding 5 cc. of 10% sodium hydroxide solution and 5 cc. of 95% alcohol and evaporating to dryness on the water bath. The residue was treated twice with 5 cc. of 95% alcohol and taken to dryness, 5 cc. of water then added, potassium permanganate added to the hot aqueous solution and the analysis carried out as usual. The following results were thus obtained:

Subst., (I) 0.2979, (II) 0.2128; cc. 0.1 N $AgNO_3$, (I) 10.20, (II) 7.32.
Calc. for $C_{20}H_4I_4Cl_4O_4(COC_6H_5)_2$: I, 43.47. Found: (I) 43.46, (II) 43.66.

Action of Dry Ammonia on Tetraiodophenoltetrachlorophthalein.—When a sample of the pure tetraiodophenoltetrachlorophthalein was placed in dry ammonia it assumed a blue-green color almost immediately. A weighing in 15 minutes showed that the sample had taken up 3 molecules of ammonia. Several hours in contact with ammonia were re-

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quired, however, for the substance to come to constant weight when a total of 4 molecules of ammonia had been taken up.

Subst., 0.3121; gain in weight, 0.0208.
Calc. for $C_{20}H_8I_4Cl_4O_4.4NH_3$: NH_3, 6.63. Found: 6.25.

The salt loses 2 molecules of ammonia in half an hour in a desiccator over calcium chloride. The remaining 2 molecules are not entirely given up on standing in the desiccator for 10 days, but are lost when the salt is heated to 60° for 3 hours in a current of dry air. The material becomes colorless when all the ammonia is lost.

The Visible and Ultra-Violet Absorption Spectra of Phenolphthalein and Some of Its Halogen Derivatives.

The compounds whose spectra were determined are phenolphthalein, phenoltetrachlorophthalein and the derivatives of these 2 compounds obtained by substituting 4 bromine or iodine atoms for hydrogen in the phenol residues. The compounds used had been purified and were shown to be pure by analysis. Since the alkaline solutions are more or less sensitive to carbon dioxide, precautions were taken to exclude this gas from the solutions used.

The spectral determinations were made and the curves plotted by Drs. H. E. Howe and K. S. Gibson of the Physics Department of Cornell University and the results published in the *Physical Review, N. S.*, **10**, 767 (1917). From a study of the curves and tables the following summarized statement of facts may be made:

Neutral alcoholic solutions of the phthaleins studied have absorption spectra of the same type.

The type of absorption changes when the solution becomes alkaline. In some cases the change in type can be followed through a transition stage.

The absorption of the aqueous alkaline solutions is of the same type as that of the alcoholic. The characteristic spectrum of the alkaline solutions consists of 3 absorption bands, one in the visible in the region 1600–1800, the other two in the ultra-violet, one in the region 2500–2700, the second in the region 3200–3600.

The magnitude of the absorption in the visible band and in the band near 2600 varies greatly with the phthalein, and is considerably greater in the aqueous than in the alcoholic solutions; the magnitude of the absorption in the band near 3200 is practically the same for all solutions, both aqueous and alcoholic.

Band centers have lower frequencies for alcoholic than for aqueous solutions.

Bromine and iodine in the phenol residues shift all bands toward lower frequencies.

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Chlorine in the phthalic acid residue shifts the visible band in the same direction, but shifts the two ultra-violet bands in the opposite direction.

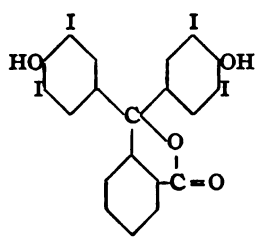
Chlorine adds a shoulder to the band in the visible on the side toward higher frequency. In the case of the neutral solutions, it adds a shoulder on the side toward lower frequency.

The shifts of the band in the visible are less in alcohol than in water.

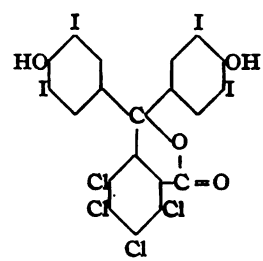
The shift increases with the mass of the substituent.

Theoretical.

Classen and Löb represent the 4 iodine atoms in tetraiodophenolphthalein as replacing 2 hydrogen atoms in each of the phenol residues. Since halogens substitute in the ortho and para positions in phenol it seems probable that, as the para positions are occupied, the iodine atoms take up the ortho positions with reference to the hydroxyl groups. In tetraiodophenoltetrachlorophthalein the iodine atoms must be in combination with the phenol residues as the hydrogen atoms of the phthalic acid residue are all replaced by chlorine. Here, too, the iodine probably takes up the ortho positions with reference to the hydroxyl groups. The two compounds are both colorless and may be represented by the following formulas:



Tetraiodophenol-phthalein.



Tetraiodophenol-tetrachlorophthalein.

Rupp[1] designates the compound obtained by the condensation of tetraiodophthalic acid and phenol as tetraiodophenolphthalein. The name phenoltetraiodophthalein for this compound would be more in harmony with the accepted nomenclature for the phthaleins.

It is interesting to note that although tetraiodophenolphthalein and tetraiodophenoltetrachlorophthalein contain 61.77% and 67.68% of halogens, respectively, they conduct themselves chemically like phthaleins and form derivatives similar to those of phenolphthalein.

Contrary to the statement of Classen and Löb, tetraiodophenolphthalein does not form a carbinolcarboxylic acid. The monopotassium and disodium salts of such an acid have, however, been obtained. These salts are colorless and may be represented by the following formulas:

[1] *Chem. Zentr.*, 15, 1058 (1911).

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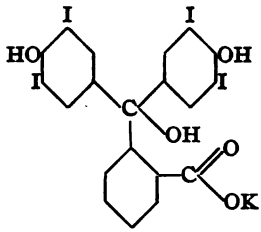
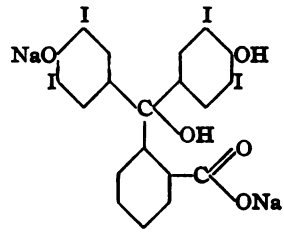
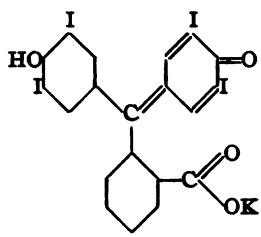


Monopotassium salt of the carbinol acid.

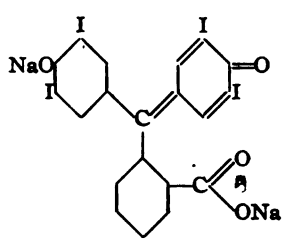


Disodium salt of the carbinol acid.

The monopotassium salt, when heated, loses water forming the green monopotassium salt of tetraiodophenolphthalein.



The disodium salt crystallized from alcohol loses both alcohol and water when heated, forming the blue disodium salt of tetraiodophenolphthalein. Classen and Löb represent this latter compound as being formed by the replacement of the phenolic hydrogen atoms by the metal. Since the salt is colored it is best represented as having a quinoid structure.



This blue salt is quite stable in air, showing tetraiodophenolphthalein to be a stronger acid than phenolphthalein.

Both the phthaleins react with gaseous ammonia forming colored ammonium salts. While a maximum of 4 molecules of ammonia are taken up 2 of these are given up very readily and the remaining 2 more slowly. Even the diammonium salts are unstable, however, for all of the ammonia is lost on standing and the colorless phthalein results. The successive steps in the formation of polyammonia salts are given by Orndorff and Hitch.[1] The tetraammonia salts may be represented as follows:

[1] This Journal, 36, 717, 722 (1914).

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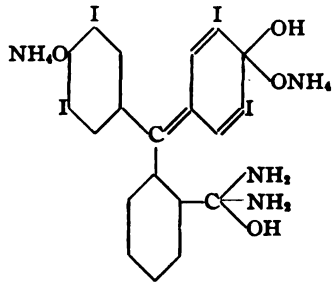
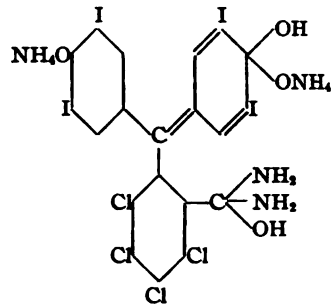
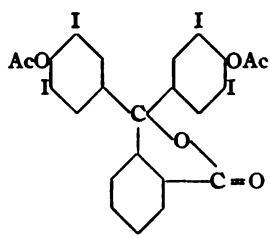


Tetraammonia salt of tetraiodophenolphthalein.

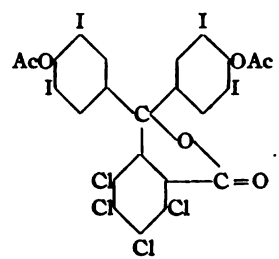


Tetraammonia salt of tetraiodophenoltetrachlorophthalein.

The diacetates and dibenzoates of tetraiodophenolphthalein and tetraiodophenoltetrachlorophthalein are colorless compounds and hence have lactoid structures.



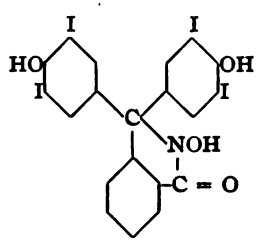
Diacetate and dibenzoate of tetraiodophenolphthalein.



Diacetate and dibenzoate of tetraiodophenoltetrachlorophthalein.

Tetraiodophenolphthalein reacts with hydroxylamine to give an oxime which is colored.

The oxime would therefore have the following formula:[1]



The results of the spectral determinations confirm the work of Meyer and Marx and Meyer and Fischer on phenolphthalein and tetrabromophenolphthalein and show an additional band in the ultra-violet which those investigators did not detect.

The neutral alcoholic solutions of all 6 phthaleins show the same type

[1] THIS JOURNAL, 39, 689 (1917).

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of absorption in the ultra-violet indicating that these compounds have similar structures.

In the alkaline solutions, both alcoholic and aqueous, the type of absorption in the ultra-violet is different from that of the neutral solutions showing that the phthaleins have undergone a change in constitution. The alkaline solutions, with the exception of tetraiodo- and tetrabromophenolphthaleins, have decided color and in these two cases the apparent absence of color is probably due to the thinness of layer and dilution of the solution necessary to allow the transmission of the ultra-violet light.

The absorption of the alkaline solutions, in the visible region is of the same type for all solutions indicating a similarity in constitution of the salts in solution. As was found in the cases of fluorescein and its halogen derivatives[1] and of the orcinolphthaleins and their halogen derivatives,[2] the introduction of halogens into the molecule shifts the absorption bands toward the red end of the spectrum and the shift is approximately proportional to the number of the halogen atoms introduced rather than to the molecular weight of the substituents.

Summary.

The results of this investigation may be briefly stated as follows:

1. Pure tetraiodophenolphthalein has been prepared and studied. It has been shown not to form a carbinolcarboxylic acid, but colorless salts of such an acid have been obtained. When these salts are heated they lose water or water and alcohol and give the colored salts of the phthalein.

2. A colorless diacetate and dibenzoate and a colored oxime have been made.

3. Tetraiodophenoltetrachlorophthalein has been made and studied. This compound is colorless and yields a colorless diacetate and dibenzoate.

4. The action of ammonia on these 2 phthaleins has been investigated.

5. The absorption spectra of phenolphthalein and some of its halogen derivatives have been studied and the absorption curves plotted.

[CONTRIBUTIONS FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, No. 310.]

A STUDY OF THE GLUCOSAZONE REACTION.

BY IRA D. GARARD AND H. C. SHERMAN.

Received February 4, 1918.

Introduction.

Since Fischer[3] first carried out the osazone reaction in 1884, it has been applied to analytical problems by numerous workers, among whom may be

[1] THIS JOURNAL, 36, 680 (1914).

[2] *Ibid.*, 37, 1201 (1915).

[3] Fischer, *Ber.*, 17, 579 (1884). See also *Ibid.*, 20, 821 (1887).

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mentioned Scheibler,[1] Jacksch,[2] Laves,[3] Maquenne,[4] Lintner and Kröber,[5] Mulliken,[6] and Sherman and Williams.[7] In his first paper, Fischer[8] pointed out that the reaction is a better test for dextrose than the common alkaline metal reductions. The later workers have varied the conditions more or less and made various applications of the reaction.

Few attempts have been made to study the reaction except for specific cases which confronted the various workers, and even within these limits the results reported in the literature are not always concordant.

The purposes of the present work are to determine definitely and somewhat fully the conditions affecting the glucosazone reaction, and the effect of some substances other than glucose; and if possible to improve the method for the detection of glucose, especially when it is present in very small amount with a large amount of some other carbohydrate.

Experimental.

Apparatus, Reagents and Procedure. Phenylhydrazine.—This was used in the form of the free base. It was prepared from the hydrochloride by the addition of saturated sodium hydroxide and then extraction several times with ether. The ethereal solution was dried over solid sodium hydroxide, decanted and the ether removed by distillation on a water bath. The phenylhydrazine was then distilled under a pressure of 20–30 mm. The reagent was prepared in 30 g. lots, since it does not keep when exposed to air.

Glucose.—Merck's "Highest Purity" glucose was used; upon analysis it showed

Moisture, 0.05%; ash, 0.01%; $[\alpha]_D$, 52.42°.

Maltose.—Merck's "Pure" maltose was obtained. It gave $[\alpha]_D$, 130.6°; reducing power, 97.92%; moisture, 0.63%; and so further purification was necessary. The method of Baker and Day[9] was used. The maltose was dissolved in a small volume of water, cooled and poured into enough 95% alcohol to give a final concentration of 85%. It was then filtered, seeded and stirred occasionally for 2 days, when it had crystallized. The process was repeated and the product dried at 70° in a vacuum oven.

$[\alpha]_D$, 137.1°; moisture, 0.4%; ash, 0.065%.

[1] Scheibler, *Ber.*, **17**, 1729 (1884).

[2] Jacksch, Vaubel's *Bestimmung organisher Verbindung*, **2**, 304 (1902); *Z. klin. Med.*, **11**, 20; *Z. anal. Chem.*, **24**, 478 (1885).

[3] Laves, *Z. anal. Chem.*, **33**, 226 (1894); *Arch. Pharm.*, **231**, 366 (1893).

[4] Maquenne, *Compt. rend.*, **112**, 799 (1891).

[5] Lintner and Kröber, *Z. gesammte Brauwesen*, **19**, 153 (1895).

[6] Milliken, *Identification of Pure Organic Compounds*, Vol. I.

[7] Sherman and Williams, THIS JOURNAL, **28**, 629 (1906).

[8] Fischer, *Loc. cit.*

[9] Baker and Day, *Repts. Brit. Assoc. Adv. Sci.*, Dublin, **1908**, p. 671.

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Lactose.—Merck's lactose was recrystallized from hot water, $[\alpha]_D$, 52.3°.

Sucrose.—Well crystallized granulated sugar, $[\alpha]_D = 66.4°$, was used.

Acetic Acid.—Kahlbaum's "C. P." acid was used without further purification.

Sodium Acetate.—"C. P." sodium acetate was used.

Apparatus.—All experiments were carried out in 50 cc. beakers, which were 7 cm. high and about 4 cm. in diameter. These were closed with a cork through which there was a hole about 2–3 mm. in diameter. The small beakers were suspended by means of a wire holder in a liter beaker of boiling water.

The melting points were taken by means of a capillary tube attached to a thermometer in a Thiele melting-point tube filled with conc. sulfuric acid.

All quantitative apparatus used was first calibrated.

Procedure.—Determinations made by Lintner and Kröber,[1] by Maquenne,[1] and by Williams[2] were checked in some cases, but in general a greater yield was obtained. It was found that the literature very seldom mentions the purity of the sugar used and in most cases the conditions were described inadequately. As was found later, the reaction is not complete in 3 hours. For these reasons, it is very difficult to obtain concordant results which check those recorded in the literature. After these observations, an attempt was made to standardize the conditions of the reaction.

The purity of the osazone precipitate was determined from its melting point. Since the melting point of phenylglucosazone is reported from 205° to 230°,[3] it was necessary to establish this constant. Two methods of purification were used: (*a*) that of Fischer, according to which a sample was recrystallized from 60% alcohol, by heating, filtering and cooling; (*b*) that of Tutin,[4] following which the osazone was dissolved in pyridin, and then alcohol, and finally water was added to precipitate it. After 3 recrystallizations by either method, the melting point was 207.9° when the temperature was raised 1° in 2 to 3 seconds as recommended by Fischer.[5] He obtained 208.0°, but Tutin had maintained that when pyridin was used for the recrystallization the value was 217.0°. All melting points taken in this work are given "corrected" as the room temperature and apparatus have a large influence on the result as read.

[1] *Loc. cit.*

[2] Williams, Unpublished.

[3] LeCoff, *Compt. rend.*, 127, 817 (1898).

[4] Tutin, *Proc. Chem. Soc.*, 23, 250 (1907).

[5] Fischer, *Ber.*, 41, 73 (1908).

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Concentration of the Reagent.—In order to establish the concentration of the reagent necessary to produce a maximum yield of osazone a series of determinations were made. In each case a sample of 0.2 g. glucose in a total volume of 20 cc. was heated for 1.5 hours at 100°. The precipitate was collected on a paper in a Gooch crucible, washed with five 10 cc. portions of water at room temperature, dried at 100° and weighed. 0.4, 0.6, 0.8, 1.0, 1.5, 2.0, 2.5, 3.0, and 3.5 g. of phenylhydrazine with an equal weight of glacial acetic acid in each case was used and 4 of the determinations in the vicinity of the maximum were repeated. From the results which are shown graphically in Fig. 1, it is seen that a maximum is reached when the concentration of phenylhydrazine lies between 1.0 and 1.2 molar, *i. e.*, about 2.0 g. in 20 cc. From this it falls off until at 1.6 *M* it is only 42.4% of the theoretical.

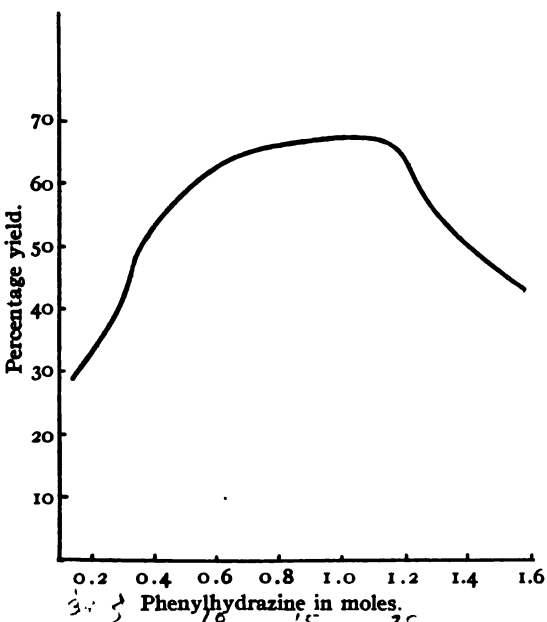

Fig. 1.—Influence of concentration of reagent upon the yield of phenylglucosazone.

Three factors may enter here: the quantity or concentration of phenylhydrazine, the acidity of the reagent, and the nature of the solvent, or rather the solubility of the osazone in the solvent which changes with the increasing percentage of acid and base present, and the resulting decrease of water. The increasing yield is undoubtedly due to the increase of concentration of the phenylhydrazine up to about 2 g. of phenylhydrazine in a volume of 20 cc. At this concentration, the phenylhydrazine acetate is about 0.92 *M* and the excess of acetic acid is 0.73 *M*. The decline in yield shown by the curve may be due either to the increased acidity or to the increased solubility of the osazone in the reagent. The first alternative was investigated by testing the acidity colorimetrically. The increase in acidity was found to be very slight. This was to be expected, however, since the presence of the acetate acts as a "buffer" to the acid. Furthermore, a test with 0.92 *M* phenylhydrazine and 3.33 *M* acid or an excess of 2.4 *M* gave a yield of 53%, which shows that any decrease in yield due to the acidity is much smaller than that observed

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above. No attempt was made to determine the solubility of the osazone in the mother liquor, due to the complexity and variation of the solvent. Some observations, however, indicate that the loss is due to secondary effects of the reagent. As the reagent became more concentrated, the precipitate became more and more discolored which indicates decomposition. The melting point in these cases was lower, which shows that the product is less pure. The mode of precipitation was also very different from that in more dilute solutions. The precipitate did not form so soon and came out very much slower after the first crystals began to appear.

In the light of these observations and Laves[1] results with the solubility of phenylglucosazone, it seems evident that the decrease in yield with an increase in concentration of the reagent beyond a molar solution is due to the destructive action of the reagent and the increasing solubility of the precipitate in the reagent.

Acidity.—It was thought desirable to investigate the effect of (*a*) the negative ion of the acid, (*b*) the quantity of acid used, (*c*) the actual acidity, and (*d*) the presence of a salt of a weak acid on the course of the reaction. In order to establish the first point several different acids were used. Some difficulty was experienced in obtaining suitable acids, since those of the desired strength are organic acids which were in some cases not available and in others were not sufficiently soluble. However, the following table gives a list of acids with constants which differ sufficiently for the purpose. The reactions were carried out with 0.2 g. glucose in a volume of 20 cc. and varying proportions of the acid and base. The yield is reported at the end of 1.5 hours. The constants are given at 25° for the sake of uniformity as the values at 100° in some cases are not available. The results were as given in Table I.

In addition to the results tabulated, a series of determinations were made with the concentration of the base equal to 0.92 *M* and the acetic acid varying by steps from 1.66 *M* to 4.58 *M*. In each case 0.2 g. glucose in a volume of 20 cc. was heated with the reagent for 1.5 hours. The resulting graph (Fig. 2) shows that a maximum is reached when the solution is slightly acid, *i. e.*, with a base concentration of 0.92 *M* and acid of 2.08 *M*. If the acid is increased beyond this point, the yield decreases and the solutions become badly discolored which indicates decomposition. It is found that a concentration of acid is soon reached at which there is no precipitation. The graph shows that the range of acidity within which the reaction takes place is very small. The fact that the maximum yield is reached in acid solution is probably due to the removal of NH_3 and $C_6H_5NH_2$ by the acid to form NH_4^+ and $C_6H_5NH_3^+$, respectively. These tabulated results indicate that the yield is a func-

[1] *Loc. cit.*

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TABLE I.—EFFECT OF THE ACIDITY OF THE REAGENT ON THE YIELD OF OSAZONE.

Phenylhydrazine. G.	Acid G.		Dissociation constant of acid.	Sodium acetate.	P_H+.	Yield % theory.
1.0	....		....	...	..	0.0
1.0	Phenol	1.0	1.3×10^{-10}	...	..	0.0
1.0	Boric	0.33	6.6×10^{-10}	...	..	0.0
0.4	α-Naphthol	0.4	1.0×10^{-8}	...	..	0.0
1.0	NaH_2PO_4	1.0	2.0×10^{-7}	...	..	31.2
1.0	Succinic	0.6	6.6×10^{-6}	...	..	40.0
1.0	Succinic	0.5	6.6×10^{-6}	...	..	44.13
1.0 HCl salt	....		1.0 (?)	...	..	0.0
0.5 HCl salt in 10 cc.	....		1.0 (?)	...	4.1	0.0
0.5 in 10 cc.	....		....	...	6.0	0.0
1.0 in 20 cc.	Acetic	1.0	1.8×10^{-5}	...	4.6	53.32
2.5 in 20 cc.	Acetic	2.5	1.8×10^{-5}	...	4.8	71.35
3.0 in 20 cc.	Acetic	3.0	1.8×10^{-5}	...	4.6	53.15
0.4 in 10 cc.	Acetic	0.5	1.8×10^{-5}	0.5	4.7	75.9
0.5 in 10 cc.	Acetic	0.5	1.8×10^{-5}	0.5	4.85	73.72
0.5 in 10 cc.	Acetic	0.625	1.8×10^{-5}	0.5	4.5	75.9
0.4 in 10 cc.	Acetic	0.5	1.8×10^{-5}	0.5	4.7[1]	...
0.5 in 10 cc.	Acetic	0.5	1.8×10^{-5}	0.5	4.85[1]	...
0.5 in 10 cc.	Acetic	0.625	1.8×10^{-5}	0.5	4.8[1]	...

tion of the acidity and independent of the negative ion of the acid used. The constants show the relative strength of the acids and the maximum acidity possible in each case. For values less than 10^{-7}, no precipitate is produced. Hydrochloric acid gives no precipitate when used alone, but as is well known, gives various yields when its acidity is reduced by means of a salt such as sodium acetate.

A constant of 10^{-5} seems to furnish hydrogen-ion concentration of the desired range. Any stronger acid may be used if its acidity is reduced by the use of a salt of a weak acid. This method has been very generally employed. However, the acidity is more difficult to control than where a weak acid is used.

Acetic acid is the most desirable since it is strong enough, may be regulated readily and is easy to obtain. This acid was chosen for the above reasons and the optimum acidity which was determined is shown by Fig. 2.

The hydrogen-ion concentrations were measured in several cases. The determination was made by the colorimetric method of Clark and Lubs. Since the solutions are somewhat yellow, the method consisted of using a tube of the solution behind the standard and a tube of water behind the one containing the solution and indicator. In this way compensation for the color of the solution was secured. The values are expressed as the P_H+ of Sorensen, *i. e.*, 0.0002 M $H^+ = 2 \times 10^{-4}$, or $P_H+ = 3.7$. Differences of 0.2 were easily noticeable which makes it possible

[1] Acidity determined after the reaction had proceeded for 1.5 hours.

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to estimate to within 0.1. The standards were those of Clark and Lubs,[1] consisting of potassium acid phthalate and sodium hydroxide and were checked by means of a hydrogen electrode and static hydrogen. The solutions were shaken for half an hour in contact with hydrogen gas, before the readings were taken. A description of the apparatus and method of calculating the $P_H{}^+$ for this method has been published.[2]

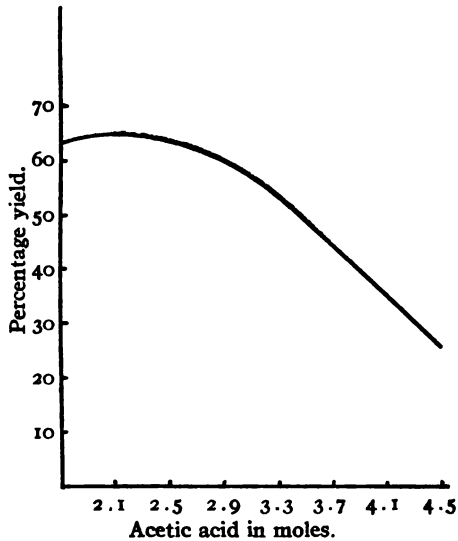

Fig. 2.—Influence of concentration of acetic acid upon yield of phenylglucosazone.

When the electrometric method was tried with solutions of the reagent directly, it was found that it did not give concordant results with these mixtures. Since the acidity does not change greatly upon heating for an hour or more, this result is probably due to the effect of the reagent on the platinum black.

The colorimetric method was much more successful, although probably not so delicate. Methyl red was used as an indicator and the results obtained by interpolation between the standards which differed by 0.2.

Table I also shows that the maximum range of acidity in which an osazone will precipitate is less than a range of $P_H{}^+$ value of 2.0, *i. e.*, from $P_H{}^+ = 4.0$ to $P_H{}^+ = 6.0$, since at neither of these extremes is a precipitate produced. The maximum lies very close to a $P_H{}^+$ value of 4.7. This corresponds pretty closely to the result obtained when different acids were used, since those acids which did not give an osazone precipitate could not give an acidity within this range.

In order to secure an excess of acid and still have the acidity low enough and constant, sodium acetate was added to the solutions. Two g. of the base, 2.5 g. of the acid, and 0.2 g. of sugar were used in each case. The results are shown in Table II.

The greatest yield is obtained with 2 *M* sodium acetate. This increase is undoubtedly due to the control of the acidity since the determination of ash in the resulting osazone showed that no important amount of sodium acetate is retained by the precipitate. The ash increases somewhat with the increased concentration but not nearly proportional to it. Potassium acetate and ammonium acetate gave results similar to those of

[1] Clark and Lubs, *J. Bact.*, **2**, 19 (1917); *J. Biol. Chem.*, **25**, 479 (1916).

[2] Sherman and Thomas, THIS JOURNAL, **37**, 623 (1915).

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sodium acetate and so the effect is apparently due to the concentration of acetate ion.

TABLE II.—EFFECT OF SODIUM ACETATE ON THE YIELD, MELTING POINT AND TIME OF FORMATION OF THE OSAZONE.

NaAc. *M*.	Yield. % of theory.	M. p. Degrees.	Time. Minutes.
0.0	65.00	205.0	7.5
0.25	68.60	209.0	5.0
0.5	68.48	210.5	7.5
1.0	69.23	210.5	7.5
2.0	71.65	209.5	10.0
3.0	69.48	Not taken	14.0

The volume of the reacting mixture was investigated and the following results obtained:

TABLE III.—EFFECT OF THE VOLUME IN WHICH THE REACTION TAKES PLACE ON THE YIELD OF OSAZONE.

Volume. Cc.	Glucose. Mg.	Yield. % of theory.
30	200.0	65.6
30	5.0	33.0
20	200.0	76.8
20	5.0	44.5
10	200.0	84.0
10	100.0	80.4

From this it seems that 20 cc. is the best volume to use for a sample of 0.2 g. While the yield is greater in 10 cc. the amount of decomposition is also greater. However, this effect can be largely overcome by reducing the reagent also by half and thereby reducing the concentration to the original, *i. e.*, 1.0 g. phenylhydrazine, 1.25 g. glacial acetic and 0.6835 g. of crystallized sodium acetate (0.25 *M*). The greatest importance of the volume therefore, is its effect on the constant loss due to solubility of the precipitate and on the purity of the osazone.

Concentration of Sugar in the Mixture.—2.0 g. of phenylhydrazine, 2.5 g. of acetic acid and 1.367 g. of sodium acetate in a volume of 20 cc. gave, when heated for 1.5 hours, the results shown in Cols. II and III under yield in Table IV.

This series was repeated with 0.5 g. phenylhydrazine, 0.5 g. acetic acid, and 0.5 g. sodium acetate in a volume of 10 cc. heated for 2 hours, with the results shown in Col. IV.

There is a constant loss due to the solubility of the osazone in the reagent which will appear as a decreasing yield due to the fact that it is a larger percentage of the smaller sample. From the complex nature of the solvent, it is difficult to determine the exact value of this solubility but it is less than 10 mg. to 10 cc. of the reagent, since 5 mg. of glucose has a theoretical yield of 10 mg. Assuming that this is the only loss from 5 mg. of sugar, the loss is 6.5 mg.

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TABLE IV.—EFFECT OF THE CONCENTRATION OF GLUCOSE ON THE YIELD OF OSAZONE.

I. Glucose. Mg.	Yield, % of theory. Higher conc. of reagent. II.	III.	Lower conc. of reagent. IV.
200	76.95	76.7	73.72
150	75.95	...	72.43
100	71.65	71.8	70.55
50	65.6	...	68.20
20	...	...	59.5
10	48.50	49.00[1]	48.0
5	45.00	44.00[1]	35.0
2	Slight on cooling		

Wash Water.—A determination was made with 1.0 g. phenylhydrazine, 1.25 g. acetic acid, 0.6835 g. sodium acetate (0.25 *M*) in a volume of 10 cc. The whole was heated 2 hours, cooled to 60° and filtered. Wash water at room temperature was added in 10 cc. portions, collected separately and weighed, evaporated to dryness and the residue weighed, with the results shown in Table V.

TABLE V.—SOLIDS REMOVED BY SUCCESSIVE WASHINGS.

No.	Volume. Cc.	Solids. G. I.	II.	III.
1	10	0.0520	0.0532	0.0566
2	10	0.0053	0.0258	0.0182
3	10	0.0061	0.0070	0.0058
4	10	0.0025	0.0029	0.0026
5	10	..	0.0016	0.0017
6	10	..	..	0.0011
7	10	..	..	0.0004

The washing is practically complete after the fifth 10 cc. portion of water has been used. Less than 2 mg. was removed by the fifth portion and that was probably mostly osazone, as the solution was distinctly yellow. No attempt was made to analyze this residue, however, since it decomposed (became discolored) during the evaporation of the water.

Duration of the Reaction.—The time necessary for the maximum yield of osazone has been variously reported. Some of the determinations made in the course of this investigation gave the results shown in Table VI.

TABLE VI.—EFFECT OF THE DURATION OF HEATING ON THE YIELD OF OSAZONE.

Time. Hours.	Yield. % of theory.
1.0	56.9
1.5	65.9
2.0	76.5
2.5	77.0
3.0	81.0
4.0	Decomposed

[1] Molar sodium acetate was used in checks.

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The reaction is not complete in less than 3 hours. Beyond this time it is impossible to say because of the decomposition which takes place under prolonged heating. From these results, it is most desirable to heat for 2 hours since that time produces the greatest yield of a relatively pure product. The speed of the reaction like the yield is a function of the concentration of reagent used and of the acidity. In no case has the reaction been found nearly complete in less than 2 hours and in no case has a greater time seemed desirable. While a less acid solution produces less decomposition of the osazone, it also results in a slower reaction.

Application to the Detection of Single and Mixed Sugars.—The conditions which produce the largest yield with a sample of 0.2 g. are not those best adapted to detecting minute amounts of glucose. This is probably due to the fact that the osazone is more soluble in the phenylhydrazine-acetic acid mixture than it is in water. While more osazone may be formed in the case of the more concentrated reagent it does not separate out of the solution so readily. The most important results are reported in Tables VII, VIII, IX, X and XI.

TABLE VII.—EFFECT OF CONCENTRATION OF THE REAGENT ON THE TIME OF PRECIPITATION WHEN GLUCOSE IS IN 0.05% SOLUTION AND VOLUME EQUALS 10 CC.

Phenylhydrazine.	Acetic acid. G.	Sodium acetate. G.	Time.
0.6	0.4	0.5	None-hot
0.8	0.5	0.5	In 4 hrs.
0.8	0.8	0.5	None in 2 hrs.
0.6	0.6	0.5	70 min.
0.4	0.4	0.2	63 min.
0.4	0.5	0.2	50 min.
0.4	0.5	0.5	47 min.
0.5	0.5	0.5	54 min.
0.5	0.625	0.5	82 min.
0.4[1]	0.5	0.5	None in 2 hrs. or on cooling
0.5[1]	0.5	0.5	

In Table VII the results are tabulated from the experiments made for the purpose of finding the conditions necessary to determine a minimum quantity of glucose. From these and other experiments it appears that with 0.005 g. of glucose, 0.4 g. phenylhydrazine, 0.5 g. acetic acid, and 0.5 g. sodium acetate produce a precipitate in the least time. Those conditions in which the base predominates are distinctly inferior and so are discarded in future experiments. It may be noticed also that an increase in the concentration of the reagent lessens the delicacy.

In Table VIII the 3 most likely sets of conditions are compared and the limits given in each case. Here it is seen that the conditions given in the preceding paragraph are the best, while an equal weight (0.5 g.) of each of the 3 reagents is only slightly inferior. With the best condi-

[1] Volume was 4 cc. in these 2 tests only.

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TABLE VIII.—EFFECT OF THE CONCENTRATION OF GLUCOSE ON THE TIME OF PRECIPITATION WHEN A VOLUME OF 10 CC. CONTAINING 0.5 G. SODIUM ACETATE WAS USED IN EACH CASE.

Dextrose. G.	Time.
Using 0.5 g. Phenylhydrazine and 0.5 g. Acetic Acid	
0.200	6 min.
0.100	5 min.
0.010	19 min.
0.005	54 min.
0.002	None in 3 hrs.—distinct when cool
0.001	None
Using 0.4 g. Phenylhydrazine and 0.5 g. Acetic Acid.	
0.200	5 min.
0.100	5 min.
0.010	14 min.
0.005	47 min.
0.002	None in 3 hrs.—distinct when cool
0.001	Ppt. on cooling after 3 hrs. heating
Using 0.5 g. Phenylhydrazine and 0.625 g. Acetic Acid.	
0.100	6 min.
0.010	27 min.
0.005	82 min.
0.002	None in 3 hrs.—distinct when cool
0.001	None

TABLE IX.—CONDITIONS OF PRECIPITATION FROM SOLUTIONS OF SUCROSE, MALTOSE AND LACTOSE WHEN A VOLUME OF 20 CC. WAS USED WITH 1 G. OF PHENYLHYDRAZINE AND 10 CC. IN ALL OTHER CASES.

Phenylhydrazine. G.	Acetic acid. G.	Sodium acetate. G.	Time. Min.	Yield. % of theory.
Using 0.200 g. Sucrose.[1]				
0.4	0.5	0.5	30	..
0.5	0.5	0.5	33	..
0.5	0.625	0.5	29	..
1.0	0.8	1.367	85	..
1.0	1.25	0.6835	60	..
1.0	1.25	None	45	..
1.0	1.00	1.367	80	..
1.0	1.00	None	48	..
1.0	1.00	1.367	70	..
1.0	0.6	1.5	100	..
Using 0.100 g. Sucrose.[1]				
1.0	0.6	1.5	130	..
Using 0.200 g. Maltose.[2]				
0.4	0.5	0.5	...	41.8
0.5	0.5	0.5	...	40.6
Using 0.200 g. Lactose.[3]				
0.4	0.5	0.5	...	54.7
0.5	0.5	0.5	...	54.6

[1] Precipitation begins at 100°; [2] at 63°; [3] at 65° in the first and 64° in the second experiment.

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TABLE X.—EFFECT OF MALTOSE ON THE PRECIPITATION OF GLUCOSAZONE WHEN A VOLUME OF 10 CC. IS USED.

Phenylhydrazine. G.	Acetic acid. G.	Sodium acetate. G.	Maltose. G.	Glucose. G.	Time. Min.	Yield in 2 hrs.
0.5	0.5	0.5	0.050	0.150	5.5	80.26 at 70°
0.5	0.5	0.5	0.100	0.100	6.5	86.35 at 70°
0.5	0.5	0.5	0.150	0.050	8.0	70.40 at 70°
0.5	0.5	0.5	0.180	0.020	29.0	54.25 at 70°
0.5	0.5	0.5	0.190	0.010	None-hot	5.0 at 70°
0.5	0.5	0.5	0.195	0.005	None-hot	....
0.4	0.5	0.5	0.180	0.020	40.0	51.25
0.4	0.5	0.5	0.190	0.010	None in 4 hrs.	....
0.4	0.5	0.5	0.190	0.010	None in 4 hrs.	....
0.5	0.5	0.2	0.190	0.010	None in 4 hrs.	....
0.5	0.625	0.5	0.190	0.010	None in 4 hrs.	....
0.5	0.5	0.5	0.150	0.050	10.0	....
0.5	0.5	0.5	0.180	0.020	35.0	....
0.5	0.5	0.5	0.180	0.020	34.0	40.0[1]

tions it is possible to detect 5 mg. of glucose in 10 cc. of solution since a distinct precipitate is formed. If the solution is cooled, 1 mg. gives a distinct precipitate. If the original solution is neutral and comparatively free from other organic matter this test will show 1 part of glucose in 10,000 of water or 1 mg. in a 0.01% solution. At this dilution the precipitate is sufficiently copious, so that there is no question about its presence.

Since it is sometimes necessary to determine glucose in the presence of sucrose, the experiments reported in Table IX were made. As is well known, sucrose forms a glucosazone because it is hydrolyzed by the acid character of the reagent mixture. It is possible to reduce the acidity until sucrose will not be sufficiently hydrolyzed to give a precipitate on being heated for over an hour when 0.2 g. is present. These same conditions will give a precipitate with glucose in a few minutes. Table IX also shows the effect of sucrose when it is in a mixture. With small amounts of sucrose, the time required for the precipitate to form is not greatly changed, while with 2.5% glucose the time of formation of the precipitate shows that the sample is not pure sucrose.

Some cooling below 100° is unavoidable during filtration and so determinations were made with lactose and maltose to find at what temperature they begin to give a precipitate. The results show that no danger from this source is met with, so long as the temperature is kept above 70°, since maltosazone and lactosazone do not begin to crystallize until the solution is cooled to about 65°. If the filtration is carried out promptly the solution may be kept much above this temperature.

The effect of these sugars on the glucosazone reaction (maltose in Table X, lactose in Table XI) is to retard it, as has been shown by former

[1] Cooled to room temperature and reheated.

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TABLE XI.[1]—EFFECT OF LACTOSE, SUCROSE, STARCH AND DEXTRIN ON THE PRECIPITATION OF GLUCOSAZONE.

Lactose. G.	Glucose. G.	Time. Min.	Yield in 2 hrs.
0.150	0.050	14	....
0.180	0.020	45	....
0.180	0.020	46	....
0.000	0.020	18	....
0.050	0.150	5	72.2%
0.100	0.100	7.5	70.35%
0.150	0.050	13	63.90
0.180	0.020	39	22.75
0.190	0.010	...	1.0(?)[2]
Sucrose.			
0.050	0.150	4.5	78.73%
0.100	0.100	5.5	81.55
0.150	0.050	7.0	95.8
0.180	0.020	13.0	150.5
0.190	0.010	23.0	245.0
0.195	0.005	28.0	409.0
Starch.			
0.050	0.150	5.0	71.30%
0.100	0.100	6.0	69.35
0.150	0.050	8.0	67.00
0.180	0.020	16.0	58.50
0.190	0.010	36.0	47.0
0.195	0.005	120.0?	14.0
Dextrin.			
0.050	0.150	5	67.6%
0.100	0.100	7	(45.5)
0.150	0.050	13	66.5
0.180	0.020	28	59.2
0.190	0.010	...	71.5
0.195	0.005	...	70.0

workers. With 90% maltose and 10% glucose the time is retarded from 15.5 min. to 28 min. With 95% maltose and 5% glucose, no osazone is formed unless the solution is cooled. Some of this precipitate does not redissolve on reheating. Since all maltosazone and lactosazone dissolve on heating this residue must be glucosazone and so if the sample is a mixture of maltose and glucose, 5% glucose is the minimum limit of this reaction. Heating for a greater length of time does not give a precipitate with the 5% glucose in the presence of 95% of either maltose or lactose.

The effect of lactose is seen to be greater than that of maltose, as was reported by Sherman and Williams.[3] While 90% maltose retards the

[1] Reagent is 0.5 g. phenylhydrazine, 0.5 HAc, 0.5 g. NaAc in a volume of 10 cc. None were discolored with starch present.

[2] Cooled to room temperature and reheated.

[3] *Loc. cit.*

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precipitation to 29 min. the 90% lactose retards it to 45 min. With lactose the minimum limit of the reaction is the same, under the conditions here used, as with maltose, *i. e.*, 10% hot, and 5% by cooling and reheating, was the smallest proportion of glucose in lactose which gave a satisfactory test.

As the concentration of the reagent increases, the time required for precipitation of the osazone increases. As has been suggested at an earlier point, this is due to the fact that the osazone is more soluble in the reagent than it is in water and that it crystallizes out more slowly. In view of this, the retarding effect of disaccharides is apparently due to the presence of their osazones and not, as has sometimes been supposed, to the reduced concentration of the reagent due to its removal to form the disaccharide osazones. This view is further supported by the fact that the retarding effects of equivalent quantities of maltose and lactose are not the same.

The effect of starch is peculiar. The time of precipitation is only slightly less. With less than 50% starch it may be neglected altogether. The precipitates were less discolored than when no starch was used, and the yield was very little affected.

The effect of dextrin is very similar to that of maltose. This is especially noteworthy from an analytical standpoint, since both are likely to be present in the same solution.

A knowledge of the effects of the various factors above recorded makes it possible to interpret the results of an osazone reaction in a wider variety of cases than has been possible heretofore. In the interpretation of a given result, the yield, the melting point of the osazone, and the time required for the formation of a precipitate should, in general, be employed. There are cases, however, where merely the formation of a precipitate is conclusive. In order to avoid erroneous conclusions, it should be borne in mind that pentoses as well as other hexoses affect the results obtained.

The reaction was applied to one analytical problem. Starch had been hydrolyzed by an enzyme (taka-diastase) and it was desirable to know whether or not glucose was formed by the reaction. 8 cc. of the solution was added to 0.5 g. of phenylhydrazine, 0.5 g. acetic acid and 0.5 g. sodium acetate. The mixture was heated for 2 hours, filtered hot, and washed with 40 cc. (4 × 10 cc.) of distilled water at room temperature. The time was taken in each case and the yield in 3 of them.

TABLE XII.—GLUCOSAZONE PRECIPITATION FROM UNKNOWN SOLUTIONS.

Solution No.	Time. Min.	Yield. Mg.	Glucose. Mg.
3	12	15.0	12.7
4	31	13.3	11.6
7	10	..	..
8	5(?)	7.5	7.6(?)

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From these results it is obvious that all of the samples contain glucose and some idea is obtained of the amount of it. From Table IV it is seen that if 4.0 mg. are added to the weight of osazone formed in a given case, the yield is then about 75% of the theoretical, or 1.5 times the weight of glucose. From this it is possible to calculate arithmetically the quantity of glucose, *i. e.*, $\frac{\text{mg. of osazone} + 4.0 \text{ mg.}}{1.5} = \text{mg. of glucose}$. At this dilution, however, the percentage yield is not very reliable, since small losses affect the result greatly. It does serve to establish a minimum quantity of glucose, since neither maltose, starch, nor dextrin yields any precipitate when treated in a similar manner. If the time is considered it will also serve to establish a minimum glucose content. The precipitate from solution No. 4, Table XII, came down in 31 minutes. With pure glucose this would mean about 10 mg. of glucose, but with 75 mg. of maltose present the precipitation is retarded and so the quantity of glucose is much in excess of 10 mg.

Conclusions.

1. The correct melting point of phenylglucosazone is 208.0° (corr.) regardless of the method of purification.

2. There is a concentration of phenylhydrazine which produces a maximum yield of glucosazone; any increase in the concentration above this results in a rapidly decreasing yield, probably due to the increased solubility of the osazone in the reagent.

3. The efficiency of the reagent depends upon the acidity and is independent of the negative ion of the acid used.

4. The range of acidity in which the reaction takes place is rather slight, between $P_{H^+} = 4.0$ and 6.0. The maximum lies close to 4.7 and is best secured with acetic acid and sodium acetate. Very slight change in acidity takes place during the reaction.

5. Within fairly wide limits a variation of the size of the sugar sample used has very little effect on the percentage yield of osazone beyond the effect due to the constant loss which results from the solubility of the osazone.

6. With such quantities of sugar and reagents as were here used, 4 10 cc. portions of water at room temperature wash the precipitate sufficiently for analytical purposes.

7. While maltose and dextrin retard the formation of the precipitate, lactose retards it to a greater extent and starch has very little effect.

8. The limit of the delicacy of the test for glucose has been extended.

9. The tabulated results of experiments with both pure sugars and mixtures extend the analytical application of the reaction.

10. The reaction continues at least three hours.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON UNIVERSITY.]

ON THE PREPARATION OF FUMARIC NITRILE.

THE ACTION OF HYDROXYLAMINE ON FUMARIC NITRILE.

BY L. McMASTER AND F. B. LANGRECK.

Received March 21, 1918.

The nitrile[1] of fumaric acid was prepared some years ago in this laboratory by heating fumaramide with phosphorus pentoxide, but the yield was very small. The constitution[2] of this nitrile was established by transforming it back into fumaramide and fumaric acid.

To inquire further into the methods of preparation and the properties of this nitrile is the purpose of this work. At first, experiments were made to improve the methods of making the nitrile and then the action of hydroxylamine upon it was studied.

Preparation from Fumaramide.

Preparation of Methyl Fumarate.—Twenty g. of pure fumaric acid was dissolved in 120 cc. of absolute methyl alcohol and the solution boiled for 8 hours on the water bath. During the heating a stream of dry hydrogen chloride was passed through the solution. After cooling, the contents of the flask practically solidified. The mass was broken up and the crystals of dimethyl fumarate were filtered off on a suction filter. They were washed with 10 cc. of ice-cold alcohol and dried by drawing air through them while on the filter. Yield, 19.5 g. of large, white, glistening leaves; m. p. 102°. The recorded[3] m. p. is 102°. This method was found to give the best yield of several tried. The alcoholic filtrate was evaporated to about 50 cc. and a second crop of crystals obtained. These, however, required a recrystallization from hot methyl alcohol to rid them of a yellowish color.

Preparation of Fumaramide.—Nine g. of the dimethyl fumarate was treated with 35 cc. of ammonia water, sp. gr. 0.90. The mixture was placed in a flask and allowed to stand, with occasional shaking, for 24 hours.[4] The fumaramide formed as a fine, white powder. It was filtered off, dried on the filter and then heated in an air bath at 110°. The filtrate, containing some unchanged ester, was saturated in the cold with ammonia gas and allowed to stand for 24 hours, whereupon further formation of the amide took place. The total yield was 6.2 g. of fumaramide which melted, after carbonizing, at 266°.

Preparation of the Nitrile.—Keiser and Kessler[5] obtained a yield of 0.15 g. of nitrile (5.6% of theory), by heating 5 g. of fumaramide with

[1] Keiser and Kessler, *Am. Chem. J.*, **46**, 523 (1911).

[2] Keiser and McMaster, *Ibid.*, **49**, 81 (1913).

[3] Anschütz, *Ber.*, **12**, 2282 (1879).

[4] See Hagen, *Ann.*, **38**, 275 (1841).

[5] *Loc. cit.*

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15 g. of phosphorus pentoxide to 120° in a crystallizing dish, covered with a cool funnel, on the walls of which the sublimate of nitrile condensed. This method was repeated a number of times, and the best yield we could obtain from 5 g. of amide was 0.16 g. of nitrile (6% of theory).

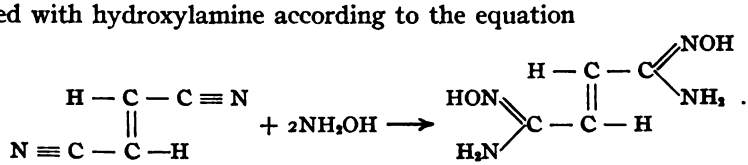
We then carried out the reaction in a retort and passed a current of dry air over the mixture to carry away the nitrile as fast as it was formed. A water-cooled condenser was substituted for the funnels. The retort was heated to 170° in an oil bath. Experiments, using 3 g. of fumaramide, gave yields of nitrile that varied from 12 to 15% of theoretical. It was now decided to carry out the reaction in the presence of dry nitrogen instead of air. The nitrogen was prepared from air by means of Van Brundt's[1] apparatus. 25% yields of the nitrile were thus obtained.

Attempts were made to prepare the nitrile by heating zinc fumarate with lead, barium and potassium thiocyanates but no yields could be obtained.

We also carried out experiments in an attempt to prepare the amide and nitrile of maleic acid. While our work on these compounds has been very much more extended than that[2] previously done in this laboratory, the results were not satisfactory.

The Action of Hydroxylamine on Fumaric Nitrile.

Fumaric nitrile, being a dinitrile, should yield a diamidoxime when treated with hydroxylamine according to the equation



Preparation.—One g. of fumaric nitrile was treated with 1.77 g. of hydroxylamine hydrochloride and 1.36 g. of sodium carbonate, dissolved in 20 cc. of water. After the evolution of carbon dioxide had ceased, a clear solution resulted. The mixture was allowed to stand 15 hours, at the end of which time a bulky, white mass had separated out of solution. After filtering, this white mass was recrystallized from hot water and formed as fine, white needles. They melted sharply, with carbonization, at 212°. At temperatures below 212°, the crystals slowly blackened and it was necessary to make the determination by plunging the m. p. tube into sulfuric acid at or near 212°. Yield, 0.32 g. This procedure was repeated a number of times.

Properties.—The substance is fairly soluble in cold water and very soluble in hot water, from which it crystallizes as slender, sparkling needles. It is insoluble in ether and cold ethyl alcohol, and but slightly soluble in

[1] This Journal, 36, 1448 (1914).

[2] Keiser and McMaster, *Am. Chem. J.*, 49, 81 (1913).

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hot alcohol. It is insoluble in chloroform and acetone and readily soluble in glacial acetic acid.

The aqueous solution gives no precipitate with potassium chromate or picric acid solutions. It gives a deep red color with ferric chloride solution, which is characteristic of amidoximes. Bromine water and alkaline potassium permanganate solution are rapidly decolorized by the aqueous solution. Silver nitrate solution precipitates a white salt from the aqueous solution. This salt, when heated, deflagrates and leaves a residue of silver.

Dry hydrogen chloride passed into the glacial acetic acid solution of the compound precipitates a white substance which is very soluble in water. This precipitate melts at 212°, hydrochloric acid being split off during the heating. Evidently the hydrochloride of the original compound had been formed.

Boiling the compound with water for 20 hours failed to transform it into fumaramide, as was expected.

Analysis.—If the compouhd is the diamidoxime and has the formula $C_4H_8N_4O_2$, it should contain 38.89% N, 33.31% C and 5.60% H. We made 5 determinations of carbon and 6 of hydrogen, each of which agreed quite well with the figures just given. We made 6 determinations of N, the results varying from 30.25% to 33.33%. The determinations were made by all the different modifications of the Kjeldahl method. Since we could obtain no check results by the Kjeldahl method, determinations of the amount of nitrogen were made by the Dumas method, which proved to be successful.

Calc. for $C_4H_8N_4O_2$: C, 33.31; H, 5.60; N, 38.89. Found: C, 33.43 (average of 5 determinations); H, 5.95 (average of 6 determinations); N, 38.55 and 38.51.

Our results of analysis check quite closely with those calculated for the diamidoxime. The compound has the solubilities in the different organic solvents characteristic of amidoximes. The other reactions mentioned are also those characteristic of amidoximes. We, therefore, are of the opinion that the new compound prepared by treating fumaric nitrile with hydroxylamine is fumardiamidoxime and has the formula given above.

If, after removing the white mass of fumardiamidoxime first formed in the reaction, we extract the filtrate with ether, there is obtained from the ether extract a yellow cotton-like substance which rapidly darkens when exposed to the air. It melts, with carbonization, at 105°. Analysis showed it to consist of 43.70% C, 6.49% H and 25.61% N.

Summary.

The method of preparation of fumaric nitrile by the action of phosphorus pentoxide on fumaramide has been improved. 25% yields, in contrast to former 6% yields, have been obtained.

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The action of hydroxylamine upon furmaric nitrile has been studied and we have prepared the diamidoxime of fumaric acid. Its properties are described.

ST. LOUIS, MO.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO.]

THE OXIDATION OF MALTOSE IN ALKALINE SOLUTION BY HYDROGEN PEROXIDE AND BY AIR.

THE PREPARATION AND STUDY OF MALTOBIONIC ACID.

BY J. W. E. GLATTFELD AND MILTON T. HANKE.[1]

Received March 25, 1918.

The work reported in this paper was begun under the direction of the late Dr. Nef and was part of the program laid out by him for solving the problem of the mechanism of the oxidation of sugars in alkaline solution. His theory of this mechanism has already been published[2] and consists, in part, of the assumptions that 1,2-, 2,3- and 3,4-di-enols, *i. e.*, $CH_2OH - CHOH - CHOH - COH = COH - CH_2OH$ (2,3-di-enol), are formed from the ordinary hexoses under these conditions, and that these di-enols later break at the double bonds giving rise to methylene-enols which undergo oxidation to produce acids. To ascertain whether the same theory, which has proved adequate for the ordinary hexoses, also applies to oxidation of the disaccharides, the oxidation of maltose here reported, was undertaken. The results are in complete harmony with the theory as far as it was possible for us to determine. That is, the presence of the oxidation products here reported can be explained by assuming that the "free" glucose unit of maltose is first enolized and the enols, after breaking, either become oxidized at once or undergo certain rearrangements with or without subsequent oxidation. An unexpected development was the discovery that a C_4-saccharinic acid was present in the oxidation mixture in the case of the oxidation with air. Up to the time of the work here reported only aldonic acids, *i. e.*, acids obtained by oxidizing the aldehyde group of aldo-monosaccharides directly to the carboxyl group, had been found in the reaction mixtures obtained in the oxidation experiments with the sugars in alkaline solutions. Although unexpected, the presence of a saccharinic acid is not unexplainable. It is well known that saccharinic acids are formed by the action of alkalies on sugars in the absence of an oxidizing agent.[3] It is therefore, quite conceivable that such acids should be formed during the oxida-

[1] The dissertation, of which this paper is a condensation, was presented by Milton T. Hanke as part fulfillment of the requirements for the degree of Doctor of Philosophy in the University of Chicago.

[2] *Am. Chem. J.*, **50**, 137 (1913).

[3] *Ann.*, **376**, 1–120 (1910).

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tion of a sugar in alkaline solution with such a mild oxidizing agent as air, when this oxidation requires 2 days for completion.

In 1914 a paper was published by Lewis and Buckborough[1] on the subject of the oxidation of maltose in alkaline solution with hydrogen peroxide. Our results are in only partial harmony with those of these authors. Their results show that the main oxidation product is glucosido-glycollic acid, while in the experiments here reported it was not possible to prove the presence of glucosido-glycollic acid. Glycollic acid was found as an oxidation product in both experiments, however, in the simple-acid fraction. From the results of the following experiments, it does not seem justifiable, therefore, to draw a final conclusion as to the structure of maltose. Much more work is necessary to show, first of all, exactly what the complete list of oxidation products of the maltose under these conditions is.

In order to get a clue as to the reason for the discrepancy between our results and those of Lewis and Buckborough, several experiments were carried out which showed that such factors as duration of oxidation and method of removing the excess hydrogen peroxide, greatly affect the results. Thus there was a decided decrease in the rotation when the glucosido acids, separated, by methods described in this paper, from the simple acids, were allowed to stand for one month with alkali and hydrogen peroxide. Furthermore, in every oxidation experiment with maltose and hydrogen peroxide, the reducing sugar had almost entirely disappeared at the end of 24 hours as shown by tests with Fehling's solution. The small amount of the remaining sugar then disappeared very slowly, so that a total of from 12 to 13 days was required to give a solution that would no longer reduce Fehling's solution.

In one set of experiments the oxidation mixtures were allowed to stand for 16 days before distillation was begun; about 16 g. of simple acids were obtained in this case. In another set of experiments the oxidation mixture stood for 13 days; approximately 13 g. of simple acids were obtained. In still another set of experiments, the oxidation mixtures stood for 21 days; approximately 20 g. of simple acids were obtained. It would seem, then, that if the oxidation were stopped at the end of 24 hours, practically no simple acids will have been formed, and the oxidation products should consist almost entirely of glucosido acids. Work, which, it is hoped, will prove or disprove this conclusion will be carried out by one of us in the future.

I. MALTOSE AND HYDROGEN PEROXIDE.

1. Experimental Procedure.

When maltose, which consists essentially of 2 *d*-glucose units, is oxidized under the conditions which pertained in these experiments, 2 classes

[1] THIS JOURNAL, 36, 2385 (1914).

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of acid oxidation products may be formed. One class consists of acids which still contain *d*-glucose units and which are called glucosido acids; the other class consists of acids which do not contain *d*-glucose units and which we shall call "simple" acids. Both glucosido- and simple acids were produced in these experiments. The first step, therefore, in the separation of the products formed, was to effect a separationin to glucosido and simple acid fractions. The next step was to effect the hydrolysis of the glucosido acids and to study the products of this hydrolysis. The final step was to separate the simple acids originally present in the oxidation mixture from each other as completely as possible.

The experimental procedure was as follows: Maltose hydrate 51.52 g., melting interval 114–130°, $[\alpha]_D^{20} = +133.4°$, was dissolved in 1280 cc. of 3% hydrogen peroxide. To this cold solution, which was vigorously shaken during the addition, was added 9 equivalents—80.7 g. of 89.2%—potassium hydroxide, dissolved in 1500 cc. of water. Enough additional water was then added to bring the total volume of the solution up to 3200 cc. The solution was allowed to stand at room temperature. The larger part of the sugar disappeared within 48 hours; but the solution was allowed to stand until it no longer had the power of reducing Fehling's solution. At the end of 13 days, the mixture was still strongly alkaline and gave an unmistakable test for hydrogen peroxide but no test for sugar. This procedure was followed in each of 3 simultaneous experiments.

The solution was then subjected to distillation under reduced pressure. Distillation was allowed to proceed at 50° until the volume of the solution was about 800 cc. This procedure removed the hydrogen peroxide completely. Hydrochloric acid —250 cc. of 5.606 *N* strength was added. The solution was again subjected to distillation and the distillate preserved. When potassium chloride began to crystallize out, distillation was interrupted and the work of determining the nature of the acids present begun.

2. The Products of Oxidation.

Formic Acid Determination.—Formic acid has usually been determined in experiments of this nature in this laboratory by a method in which the acidified oxidation liquid is subjected to complete distillation in vacuum, the distillate condensed, collected, measured and titrated with 0.1 *N* potassium hydroxide. This method is not absolutely accurate owing to loss of formic acid during the vacuum distillation. It was therefore modified as follows:

The solution was acidified and subjected to distillation in vacuum. To the end of the condenser was fitted an adapter which dipped below the surface of a measured quantity of an approximately normal solution of potassium hydroxide. After the distillation had proceeded as nearly to completion as possible, water was added to the contents of the distilling

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flask and distillation carried on to completion. The second distillate was collected in the same potassium hydroxide as the first. This process was repeated until the contents of the distilling flask no longer had a sharp acid odor. The volume of the solution in the receiver was then measured, and aliquot portions titrated with acid, and for chloride. In this way it was determined that the total amount of formic acid from 100 g. of maltose hydrate was 43.30 g.

Separation of Non-volatile Acids from Potassium Chloride.—The residue in the distilling flask was dissolved in the smallest possible quantity of water. Alcohol was then added in portions until, instead of granular potassium chloride, a slight sticky precipitate of glucosido acids appeared. The potassium chloride was collected on a suction filter and washed with 50% alcohol.

Three simultaneous experiments were carried out in this way in order to provide enough material.

Resolution of Non-volatile Acids.—The alcoholic filtrates and washings from the potassium chloride from the 3 experiments, were united and subjected to complete distillation *in vacuo*. A stiff gum was left in the flask. When this gum was dissolved in its own weight of water, and 10 times its weight of absolute alcohol was added, a copious precipitate was obtained. The aqueous alcohol was removed from the precipitate by decantation, and the precipitate was washed with absolute alcohol by decantation. This very insoluble gum, which was unquestionably glucosido acid in character, was set aside and will be referred to as the C gum.

The alcoholic mother liquor and washings from the C gum were united and subjected to distillation *in vacuo*. When the gum left in the flask was again treated according to the above procedure with water and alcohol, more soluble C gum was obtained and added to the first lot. After the combined mother liquors and washings had been subjected to distillation *in vacuo*, the gum left behind was extracted with boiling absolute alcohol and thus a third residue of C gum was obtained. In all, 47 g. of C gum, which contained some potassium chloride, was obtained.

The hot absolute alcohol extract deposited, on cooling, an apparently crystalline substance which was separated by filtration and which weighed 10.08 g. Attempts to prepare a crystalline brucine salt[1] and a crystalline

[1] To prepare brucine salts, the following procedure was invariably followed: The acid, whose brucine salt was to be prepared, was dissolved in water and treated with slightly more than the theoretical quantity of brucine, usually calculated on the basis of a titration. The mixture was heated on the boiling water bath until the brucine had dissolved and then for one hour longer. At the end of the hour, the solution was cooled and extracted 5 times with benzene to remove the excess brucine. The aqueous solution was then subjected to complete distillation *in vacuo* at 50 to 60°, and the residue, referred to in this paper as the "crude brucine salt" was recrystallized from the proper solvent.

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phenylhydrazid[1] of portions of this solid by the usual methods failed. Gums were obtained. A small portion of the solid was lost in these studies.

The mother liquor and washings from this 10.08 g. of solid, left, after distillation *in vacuo*, a gum which weighed 39.25 g. This gum was subjected to repeated alternate treatments with absolute alcohol and ethyl acetate. The ethyl acetate-soluble fractions were united. The ethyl acetate-insoluble fractions were added to the 10.08 g. of solid.

The non-volatile acid gum from the oxidation of 154.56 g. of maltose hydrate was thus divided into 3 fractions. A very insoluble glucosido acid gum called the C gum—47 g.—which was undoubtedly free from simple acids; a more soluble gum partly glucosido acid and partly simple acid—total 31.75 g.—which we shall call the B gum and which consisted of what remained of the solid, together with the ethyl acetate-insoluble gum; and a simple acid fraction soluble in ethyl acetate—11.3 g.—which we shall call the A gum.

Some experiments had been carried out in this laboratory which showed that certain acids produced insoluble basic lead salts when their water solutions are treated with a basic lead acetate solution, while other acids produce, under these conditions, soluble basic lead salts. These experiments suggested the use of basic lead acetate in effecting separations of acids such as were attempted in the work reported in this paper.

A concentrated aqueous solution of the C gum made by dissolving the 47 g. of gum in a small amount of cold water, was poured into a solution of basic lead acetate prepared by making a suspension in water of 90 g. of crystalline lead acetate and 72 g. of lead oxide, and heating the mixture until a clear solution was produced. A very heavy precipitate of basic lead salts was produced. The solution was promptly filtered and the insoluble salt washed with a large volume of water. The filtrates gave no further precipitate when treated with a fresh portion of basic lead acetate solution. The precipitated basic lead salts were suspended in water and treated with hydrogen sulfide to precipitate the lead. After having been filtered, the solution was subjected to distillation at reduced

[1] The method of preparing phenylhydrazids used by us was as follows: The acid gum, dissolved in one to two parts of absolute alcohol, was treated with a quantity of phenylhydrazine equal in volume to the amount of alcohol used. The mixture was shaken or stirred until it was homogeneous and then allowed to stand for from 1 to 24 hours according to the rapidity of the hydrazid formation. Alcohol was then added in quantities just large enough to render the mass fluid enough to be transferred to a filter, upon which the crystals were washed with small amounts of absolute alcohol and then with ether until they were white. The mother liquor and washings were subjected to complete distillation *in vacuo* at 40°. The residue was dissolved in water and this solution extracted with ether until the ether was no longer colored. The aqueous solution was then subjected to complete distillation *in vacuo* at 40° and the residue dissolved in from one to two parts of hot absolute alcohol from which a second crop of phenylhydrazid was usually deposited on cooling.

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pressure to remove the hydrogen sulfide. When this had been accomplished, distillation was interrupted and the solution treated with a suspension of freshly precipitated silver carbonate to remove the hydrogen chloride. The precipitated silver chloride was separated by filtration and the filtrate was again treated with hydrogen sulfide to remove the slight excess of silver. The filtrate and washings from the silver sulfide were subjected to complete distillation. The gum so obtained was united with a similar gum obtained from the insoluble lead salts of the B gum (see below).

The filtrate and washings from the insoluble basic lead salts from the C gum were similarly treated with hydrogen sulfide, etc., to remove the lead and hydrogen chloride. The gum finally obtained, was united with a similar gum obtained from the soluble basic lead salts from the B gum (see below).

The B gum weighed 31.75 g. It was dissolved in water and subjected to exactly the same basic lead acetate treatment as the C gum. The gums from the insoluble and soluble basic lead salts in this case seemed to be identical with the corresponding gums from the C fraction and were therefore united with those. This gave a total of 30.3 g. of gum from the insoluble basic lead salts with $[\alpha]_D^{20} + 92.52°$ and from the soluble basic lead salts, a gum which, when freed from potassium chloride, weighed 33.3 g. with $[\alpha]_D^{20} + 69.78°$.

These gums still contained some simple acids and these were removed by treating the gums with a small amount of hot absolute alcohol, precipitating most of the glucosido acids from the cold alcoholic solution with ethyl acetate, recovering the gum soluble in the alcohol-ethyl acetate mixture and extracting it repeatedly with hot ethyl acetate. There was thus removed 8.28 g. of ethyl acetate-soluble gum. This was added to the A gum which then totalled 19.5 g. with $[\alpha]_D^{20} -18.2°$. For the treatment of this gum see "The Simple Acids." The glucosido acid gum from the insoluble basic lead salt now weighed 27.2 g. with $[\alpha]_D^{20} +95.4°$ and that from the soluble basic lead salt weighed 28.3 g. with $[\alpha]_D^{20} +77.75°$. The rotations were made in 5% solutions.

The Glucosido Acids.—The gum from the insoluble basic lead salts was hydrolyzed by treatment with 130 cc. of 0.4 *N* sulfuric acid and heating for 25 hours on the boiling water bath. The sulfuric acid was quantitatively removed from the solution with barium hydroxide and the aqueous filtrate from the barium sulfate was heated at 60° for 21 hours with 6 g. of calcium carbonate. The aqueous filtrate and washings from the undissolved calcium carbonate were subjected to complete distillation *in vacuo*. The residue was dissolved in one-half its weight of water. The calcium salts were precipitated with 5 parts of absolute alcohol and washed with aqueous alcohol by decantation. To free the precipitated

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calcium salts completely from sugar, they were again dissolved in water and again precipitated and washed with alcohol. They were now transferred to a porcelain mortar by means of small amounts of hot water and enough alcohol was added to the cooled solution to precipitate them completely. The mixture of gummy salts and mother liquor was triturated until the gummy salts were transformed into a crystalline powder, which was separated by filtration, washed first with alcohol and then with ether, and finally dried *in vacuo*. The dry salts weighed 9.9 g. All the mother liquors and washings from these calcium salts were now united and subjected to complete distillation. A residue which weighed 17.5 g. and which contained the sugar produced by the hydrolysis of the glucosido acids, was thus obtained.

The gum from the soluble basic lead salts was hydrolyzed by treatment with 140 cc. 0.4 *N* sulfuric acid and heating for 25 hours on the boiling water bath. The solution was subjected to the treatment described in the preceding paragraph. There was thus obtained 11.28 g. of vacuum-dried calcium salt and 19.9 g. of crude sugar gum. The latter was added to the 17.5 g. of crude sugar gum mentioned in the preceding paragraph. This gave a total of 37.4 g. of crude sugar gum from the glucosido acids. The 2 lots of calcium salts were treated separately.

The Sugar Fraction.—The gum was dissolved in water and the solution decolorized with animal charcoal in the cold. The clear filtrate was subjected to complete distillation and yielded a nearly colorless gum. In order to free this gum from calcium salts, it was dissolved in an equal quantity of water and treated with 10 times this quantity of absolute alcohol. This treatment precipitated a gum which weighed 5 g. This gum was again taken up in water and precipitated with alcohol as before. In this way there was obtained 4.1 g. of insoluble material which, after the removal of 0.22 g. of crude *d*-arabonic phenylhydrazid, m. p. 205°, was proved by titration with Fehling's solution, to contain 1.47 g. of *d*-glucose.

The alcohol-soluble gum was recovered and subjected to a series of crystallizations in which one part by weight of water and 10 parts by weight of absolute alcohol were used. In this way, 15.60 g. of pure crystalline *d*-glucose was obtained, m. p. 149°, $[\alpha]_D^{20}$ +50.25°.

The remaining gum was oxidized in water solution by means of bromine and the acids thus formed converted into calcium salts. The crude calcium salts obtained as a residue by the distillation of the water, were recrystallized from a mixture of an equal part of water and 6 parts of 95% alcohol. This yielded 14.5 g. of salt which is proved by the following experimental data to have been calcium *d*-gluconate:

Calc. for $(C_6H_{11}O_7)_2Ca$: CaO, 13.03. Found: 13.14.
Reported for calcium gluconate: $[\alpha]_D^{20}$ +10.50°.[1] Found: +9.75°.

[1] *Ann.*, **357**, 270 (1907).

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The 14.15 g. of calcium salt is equivalent to 11.76 g. of *d*-glucose.

Of the 37.40 g. of crude sugar gum, therefore, a total of 28.83 g. were proved to have been *d*-glucose.

The Calcium Salt from the Insoluble Lead Salt Fraction.—This salt weighed 9.9 g. It was treated with the theoretical amount of oxalic acid based on an analysis for calcium oxide. The gum thus obtained weighed 7.36 g. It was treated with 800 cc. of acetone, in which 7.04 g. of gum, with $[\alpha]_D^{20}$ +7.1°, dissolved. This gum was dissolved in 14 cc. of absolute alcohol and treated with 7 cc. of phenylhydrazine. The phenylhydrazid thus formed was separated from the mother liquor by filtration and washed with absolute alcohol until pale yellow. It weighed, after having been dried in vacuum, 3.80 g. and had a melting interval of 190–194°. This phenylhydrazid was obtained from several gums discussed later and their further treatment will be found under "High Melting Phenylhydrazids" (see below).

The mother liquor and washings from the 3.80 g. of crystalline phenylhydrazid just mentioned, were subjected to complete distillation. The gum obtained was dissolved in water and the water solution was extracted with ether to remove the excess of phenylhydrazine. The gum obtained from the water solution weighed 7.46 g. It was resolved by crystallization from alcohol-ethyl acetate and alcohol-acetone mixtures into 0.15 g. of phenylhydrazid, m. p. 185–200°, which was added to the "High Melting Phenylhydrazids" (see below) and a mother liquor which is discussed under the title "The Soluble Phenylhydrazids" (see below).

The Calcium Salt from the Soluble Lead Salt Fraction.—This salt weighed 11.28 g. It was treated as the calcium salt from the insoluble lead salt had been treated. The gum obtained had $[\alpha]_D^{20}$ —16.30°. It yielded a phenylhydrazid with a melting interval of 160–185°, which weighed 3.34 g. and which was added to the "High Melting Phenylhydrazids" (see below). The mother liquor from this hydrazid was added to the "Soluble Phenylhydrazid" (see below).

The High Melting Phenylhydrazids; *d*-Arabonic Phenylhydrazid.—These weighed 7.29 g. They were recrystallized from 450 cc. of 95% alcohol. The crop of crystals weighed 4.46 g. and had a melting point of 214° $[\alpha]_D^{20}$ —14.00°, *i. e.*, 0.4000 g. dissolved in water and the solution made up to 20 cc. gave α in a 1 dcm. tube —0.28°. The recorded[1] constants for *d*-arabonic phenylhydrazid are m. p. 214°; $[\alpha]_D^{20}$ —13.90°. This phenylhydrazid was mixed with some pure *d*-arabonic phenylhydrazid. The melting point of the mixture was 214°. There can be no doubt, therefore, that the 4.46 g. of substance under consideration was *d*-arabonic phenylhydrazid.

Further attempts to obtain equally pure *d*-arabonic phenylhydrazid

[1] *Am. Chem. J.*, **50**, 144 (1913).

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from the mother liquor were failures. Crystals of much lower melting point were obtained. The entire mother liquor from the 4.46 g. of substance was therefore added to "The Soluble Phenylhydrazids" fraction.

The Soluble Phenylhydrazids; *d*-Erythronic Lactone.—The weight of the crude hydrazid obtained by subjecting the combined solutions under this head, to complete distillation *in vacuo*, was 15.1 g. The crude gum obtained from it by hydrolysis with barium hydroxide[1] weighed 8.28 g., of which 7.2 g. was soluble in ethyl acetate. This gum was somewhat mobile and in 4% aqueous solution $[\alpha]_D^{20}$ —30.00°. To remove the *d*-erythronic acid, which, according to previous indications, was undoubtedly present in this gum, the brucine salts were crystallized from absolute alcohol. In this way 21 g. of salt was obtained, which had a melting interval of 195–205°. This salt was recrystallized from a mixture of one-half its weight of water and 5 times its weight of absolute alcohol. A total of 18.15 g. of a very insoluble salt was obtained in 2 crops, melting interval 205–210°. The material in the filtrates was not identified.

The crude gum obtained by the hydrolysis[2] of the 18.15 g. of brucine salts weighed 3.95 g., of which 3.70 g. was soluble in absolute alcohol. This gum crystallized to a solid mass in the course of a few hours. In

[1] The 15.1 g. of crude phenylhydrazid was dissolved in 15 cc. of water. Fifteen g. of crystalline barium hydroxide was then added to the solution and the whole covered with a layer of toluene. The flask containing the mixture was now provided with a reflux condenser and placed on the boiling water bath. The toluene layer removed the phenylhydrazine as fast as it was formed by hydrolysis. By the use of toluene the "smearing" and loss of material, that usually accompanied such hydrolyses, was entirely avoided. Scarcely any color was developed. This mixture was kept on the boiling water bath for seven hours, then cooled. The toluene was separated, and the water solution, much diluted, extracted 5 times with ether to remove the last traces of the phenylhydrazine. The solution was now heated to boiling again, and that amount of sulfuric acid added which was necessary to precipitate all but a trace of the barium present. The barium sulfate was separated by filtration and the clear filtrate and washings subjected to complete distillation *in vacuo*. There remained, after complete distillation, 8.28 g. of crude gum. This procedure was always followed in this work in hydrolyzing phenylhydrazids.

[2] The procedure followed in hydrolyzing brucine salts was as follows: The salts were dissolved in water (example, 50 g. salts in 1500 cc. of water) and the solution heated on the boiling water bath. About $1^1/_2$ to 2 times the amount of crystalline barium hydroxide necessary to hydrolyze the brucine salts was then dissolved in water. The latter solution was also heated to boiling and added, in very small portions, to the hot brucine salt solution to which a few crystals of brucine had been added as seeds, and which was shaken vigorously during the addition. (If the barium hydroxide solution is added quite slowly, the brucine will be precipitated as a crystalline mass; if it is added too rapidly, the brucine will be precipitated as a gum, which later solidifies into balls.) When all the barium hydroxide had been added, the mixture was heated for half an hour on the boiling water bath, then cooled and allowed to stand for an hour. The brucine was then removed by filtration. The filtrate was extracted 5 times with benzol and the barium was removed with sulfuric acid.

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4% aqueous solution $[\alpha]_D^{20}$ —54.10°. It was dissolved in a small amount of hot ethyl acetate. The solution was allowed to cool, whereupon it deposited 2.1 g. of *d*-erythronic lactone, m. p. 101–103°, and $[\alpha]_D^{20}$ —70.90°; *i. e.*, 0.4598 g. of these crystals dissolved in water and the solution made up to 20 cc. gave α in a 1 dcm. tube —1.63. This solution of 0.4598 g. of crystals was titrated with 0.1 *N* potassium hydroxide. Only 0.07 cc. of the alkali was needed to bring about the first change of color in the indicator, and a total of 39.4 cc. 0.1 *N* alkali was found to have been neutralized after the solution of the lactone had been allowed to stand for one hour with an excess of alkali. The amount of 0.1 *N* alkali theoretically necessary for 0.4598 g. of a C_4-aldonic acid lactone is 39.00 cc. The recorded constants[1] for *d*-erythronic lactone are m. p. 103°, and $[\alpha]_D^{20}$ —73°. There is, therefore, no doubt that the above 2.1 g. of crystals were *d*-erythronic lactone. The material in the mother liquors from the 2.1 g. of *d*-erythronic lactone was not identified.

The Simple Acids.—The simple acids obtained from the original oxidation gum weighed 19.5 g., $[\alpha]_D^{20}$ —18.2°. This gum was entirely consumed in obtaining methods for the separation of its constituents. The simple acids whose separation is discussed here, were obtained by identical methods as above described, from another experiment.

This simple acid fraction weighed 20.22 g. and $[\alpha]_D^{20}$ —22.97°. It was treated with 40 cc. of absolute alcohol and 20 cc. of phenylhydrazine. The first crop of crystals weighed 4.5 g. and melted, with some previous softening, at 180°. From the filtrate, a second lot of crystals was obtained which weighed 0.50 g., m. p. 200°. These two lots of crystals were united and are discussed under the heading "The Crystalline Phenylhydrazids" (see below). The combined mother liquor and washings yielded a residue which weighed 29 g. This residue is discussed under the heading, "The Non-crystalline Phenylhydrazids."

The Crystalline Phenylhydrazids; Oxalic and *d*-Arabonic Acid.—These were recrystallized from 95% alcohol and gave 3.12 g. of crystals which had a melting interval of 180–193°. The mother liquor was discarded.

The 3.12 g. of crystalline phenylhydrazids were dissolved in 10 cc. of water and hydrolyzed as usual with barium hydroxide. The barium was removed by means of sulfuric acid. In order to remove oxalic acid, the presence of which had been indicated, an excess of calcium carbonate was added to the solution and the mixture heated on the boiling water bath for 5 hours. The insoluble material was then separated from the solution by filtration and examined for calcium oxalate. It was alternately dissolved in dil. hydrochloric acid and precipitated with ammonia several times. There was thus obtained an insoluble salt, which weighed, after having been dried for one hour at 100°, 0.2143 g. This salt was

[1] Ruff, *Ber.*, **32**, 3679–80 (1899).

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ignited to constant weight and left a residue of 0.0820 g. of calcium oxide.

Calc. for $CaC_2O_4.H_2O$: CaO, 38.39. Found: 38.25.

Oxalic acid was therefore present in the oxidation mixture.

The filtrate from the mixture of calcium carbonate and calcium oxalate was subjected to complete distillation *in vacuo*. There was obtained a residue which weighed 2.00 g. It was dissolved in 4 cc. of hot water. The solution was allowed to cool and deposited 1.75 g. of crystals, the analysis of which agreed with that of calcium *d*-arabonate, *i. e.*, 0.2321 g. of the salt gave on complete ignition 0.0283 g. of CaO.

Calc. for $Ca(C_5H_9O_6)_2.5H_2O$: CaO, 12.18. Found: 12.20.

The remaining 1.52 g. of calcium salt was treated with oxalic acid on the basis of the above analysis. There was obtained 0.95 g. of stiff gum which yielded by crystallization from ethyl acetate 0.62 g. of crystals. That these crystals were the lactone of *d*-arabonic was shown by a rotation and a titration. $[\alpha]_D^{20}$ +71°; *i. e.*, 0.4998 g. of crystals dissolved in water and the solution made up to 25 cc. gave α in a 1 dcm. tube +1.42. The solution which contained the 0.4998 g. of crystals was then titrated with 0.1 *N* alkali; less than 1 cc. of the alkali was necessary to produce the first change of color in the indicator, and 33.47 cc. of alkali was necessary for complete neutralization, whereas 33.75 cc. alkali is necessary theoretically for this amount of *d*-arabonic lactone.

The Non-crystalline Phenylhydrazids; Glycollic Acid.—These weighed 29 g. They were hydrolyzed with barium hydroxide in the usual way, and yielded 16.12 g. of gum which had $[\alpha]_D^{20}$ —28.55° This gum was converted into brucine salts. The crude salts were crystallized from 2 parts of absolute alcohol and 41.17 g. of salts were obtained in 3 crops which varied in melting point from 189 to 199°. These brucine salts were carefully studied but could not be identified. They yielded a gum whose $[\alpha]$ was —53°. A crystalline quinine salt and a hydrazid were made from the gum. It was finally concluded that the gum was a mixture of saccharinic acids. A study of the saccharinic acids is being made in this laboratory in the hope of throwing some light on this identification.

The mother liquor and washings from the crystalline brucine salts were subjected to complete distillation and yielded 32.8 g. of non-crystalline brucine salts. The gum obtained from these weighed 3.41 g. and had $[\alpha]_D^{20}$ —3.22°. This gum was so obviously composed largely of glycollic acid that it was at once converted into the calcium salt by heating the water solution containing the gum with an excess of calcium carbonate. The crude salt weighed 4.03 g. and yielded, as a result of recrystallization from 2 parts of water, 2.19 g. of crystalline salt. Another crop of 0.31 g. was obtained from the residue by using 50% alcohol. The mother liquors were discarded. These 3 crops were well mixed and

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then analyzed; 0.5311 g. of salt lost 0.1478 g. of water and left a residue of 0.1126 g. of calcium oxide on ignition to constant weight.

Calc. for $Ca(C_2H_3O_3)_2.4H_2O$: H_2O, 27.48; CaO, 29.47. Found: H_2O, 27.80; CaO, 29.35.

This salt was, therefore, calcium glycollate.

II. MALTOSE AND AIR.

1. Experimental Procedure.

The maltose was oxidized in 2 lots, 150 g. in all, and the oxidation products of the two lots united after the formic acid had been removed. The plan for separating the oxidation products was the same as that followed in the previous experiment. The glucosido acid gums were separated as completely as possible from the simple acid gum, and each gum then studied separately.

Seventy-five g. of maltose hydrate, m. p. 115°, $[\alpha]_D^{20}$ +131.1°, was dissolved in 1000 cc. of water. This solution was slowly added to a solution of 104.9 g. of 89.2 % potassium hydroxide (8 equivalents) in 3000 cc. of water. More water was then added to bring the final volume up to 5000 cc. A rapid stream of carbon dioxide-free air was drawn through the solution by means of the device described in a recent paper from this laboratory.[1] The water bath which surrounded the flask containing the sugar solution, was kept at a temperature of from 30 to 40° throughout the experiment. At the end of 48 hours the still strongly alkaline solution was entirely free from sugar, which indicated that oxidation was complete.

2. The Products of Oxidation.

Formic Acid Determination.—This determination was carried out before the better method of collecting the acid distillates under potassium hydroxide was introduced. A determination of the amount of formic acid produced, made precisely as indicated in the discussion of the preceding experiment except that the distillates were condensed and collected in the usual way (*i. e.*, not under potassium hydroxide), showed that 8.94 g. of formic acid per 100 g. of maltose hydrate was formed. Although this method of determination is now known to give slightly low results, it is sufficiently accurate to show that very much less formic acid was formed in the oxidation with air, than in the corresponding oxidation with hydrogen peroxide.

The Non-volatile Acids.—The residues left in the distilling flasks after the formic acid had been removed, were freed from practically all the potassium chloride in precisely the same way as in the previous experiment.

The alcoholic filtrates and washings in the 2 experiments were united, and left, after complete distillation *in vacuo*, 137 g. of gum, $[\alpha]_D^{20}$ +15°. A titration of a small portion of this gum showed that most of it was sim-

[1] THIS JOURNAL, 39, 1639 (1917).

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ple acid in character. Therefore it was subjected to extraction with a total of 2500 cc. of ethyl acetate. This caused a separation into 86.5 g. of ethyl acetate-soluble gum and 50.5 g. of insoluble gum which, when extracted with 250 cc. of hot 95% alcohol, gave 33.1 g. of alcohol-soluble gum B and 16.7 g. of insoluble gum C. The 86.5 g. of gum was then extracted with 3000 cc. of hot ether which caused a separation into 58.6 g. of ether-soluble gum $[\alpha]_D^{20}$ —17.92°, which will be referred to as "Simple Acid Gum Soluble in Ether" (see below), and 22.3 g. of ether-insoluble gum $[\alpha[_D^{20}$ +11.86°.

The B and C gums were then subjected to the basic lead acetate treatment. There was thus obtained, by a process in every detail identical with that discussed in the previous experiment, 12.45 g. of glucosido-acid gum insoluble in ethyl acetate from the combined soluble lead salts with $[\alpha]_D^{20}$ +72.50°; 10.90 g. of glucosido acid gum insoluble in ethyl acetate from the combined insoluble lead salts with $[\alpha]_D^{20}$ +94.25°; and 13.7 g. of simple acid gum soluble in ethyl acetate with $[\alpha]_D^{20}$ +19.50° to which the 22.3 g. of gum $[\alpha]_D^{20}$ +11.86° was added. This combined gum (13.78 and 22.3 g.) will be referred to as "Simple Acid Gum Insoluble in Ether but Soluble in Ethyl Acetate" (see below).

The Glucosido Acid Gums.—These gums were similar in properties to the corresponding gums from the hydrogen peroxide experiment in which it was found that there was very little difference between the acid gums obtained finally by the hydrolysis of the glucosido acids from the soluble and insoluble basic lead salts. The acid gums and sugar fractions obtained from the glucosido acid gums at present under discussion (12.45 g. and 10.98 g.) by a treatment exactly corresponding to the one discussed under the hydrogen peroxide experiment were therefore united. There were finally obtained a total of 12.98 g. of calcium salt and 14.98 g. of crystallized *d*-glucose, melting interval 149–155°; $[\alpha]_D^{20}$ +52.00°. The 12.98 g. of calcium salt was treated with oxalic acid, etc., as in the hydrogen peroxide experiment and yielded finally a very stiff gum which weighed 8.69 g., which was partially crystalline and which had $[\alpha]_D^{20}$ +18.90°. This gum was subjected to the phenylhydrazine treatment, and there was finally obtained 2.75 g. of crystalline phenylhydrazid, m. p. 198–202°, which is discussed under "The High Melting Phenylhydrazids" (see below), and 10.72 g. of non-crystalline hydrazids, which when hydrolyzed, gave 6.76 g. of gum. This gum was divided into 2 portions by extraction with acetone; a soluble gum which weighed 5.5 g. $[\alpha]_D^{20}$ +6.36°, and a tarry residue, which was discarded. The brucine salt of this gum was then made. The crude salt was separated by fractional crystallization from water and alcohol into 2 fractions; 8.31 g. of crystalline salt, m. p. 204°, and 10.30 g. of non-crystalline salt.

The Crystalline Brucine Salt; *d*-Erythronic Lactone.—The 8.31 g. of

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brucine salt was hydrolyzed and gave 1.90 g. of a very stiff, pale yellow gum, with $[\alpha]_D^{20}$ —29.40°. By careful crystallization and recrystallization from ethyl acetate, a total of 0.50 g. of *d*-erythronic lactone, m. p. 101–103°, was separated from the mixture. $[\alpha]_D^{20}$ was —71.60°; *i. e.*, 0.3126 g. dissolved in water and the solution made up to 20 cc. gave α in a 1 dcm. tube —1.12°. A titration of the same 0.3126 gram showed that only 0.04 cc. 0.1 *N* potassium hydroxide was required to cause the first color in the indicator and that a total of 26.68 cc. was required for complete neutralization. The theoretical amount required for 0.3126 g. of *d*-erythronic lactone is 26.50 cc.

The 0.50 gram of crystals was, therefore, *d*-erythronic lactone.

The Non-crystalline Brucine Salt.—This salt weighed 10.30 g. It was hydrolyzed and gave 2.13 g. of gum $[\alpha]_D^{20}$ +25.2°. The phenylhydrazid of this gum was made. There was obtained 0.45 gram of phenylhydrazid, m. p. 200°, which is discussed under "The High Melting Phenyl Hydrazids" (see below). The non-crystalline phenylhydrazid was discarded.

The High Melting Phenylhydrazids; *d*-Arabonic Phenylhydrazid.—The combined high melting phenylhydrazids weighed 3.25 g. They were recrystallized from a mixture of 150 cc. of 95% alcohol and 10 cc. of water. The first crop of crystals weighed 2.43 g., m. p. 215°; the second crop of crystals weighed 0.48 g., m. p., 214°. $[\alpha]_D^{20}$ of the two crops, well mixed, was —14.86°; *i. e.*, 0.5892 g. dissolved in water and the solution made up to 25 cc. gave α in a 1 dcm. tube —0.35°. This phenylhydrazid was mixed with some pure *d*-arabonic phenylhydrazid. The mixture melted at 214°. There can be no doubt, therefore, that the phenylhydrazid under consideration was *d*-arabonic phenylhydrazid.

The Simple Acid Fraction Soluble in Ether.—This fraction weighed 58.60 g. and had $[\alpha]_D^{20}$ —17.92°. The gum was divided into 2 parts; one part was preserved.

The part used for the study here reported weighed 28 g. It was converted into the brucine salts. The crude salt obtained was crystallized from 2 parts of absolute alcohol and yielded a total of 65.35 g. of crystalline brucine salt which ranged in melting point from 174 to 189°, and 60.33 g. of non-crystalline brucine salts.

The Crystalline Brucine Salts.—The 65.35 g. of crystalline brucine salt was hydrolyzed with barium hydroxide and yielded 11.50 g. of very soluble mobile gum, which had $[\alpha]_D^{20}$ —25°. This gum was extracted repeatedly with ether and yielded a very soluble fraction, 8.24 g., which had $[\alpha]_D^{20}$ —35°, a moderately soluble fraction, 2.30 g., which had $[\alpha]_D^{20}$ —26.5°, and a residue of 0.95 g.

The moderately soluble gum and the residue were subjected to the phenylhydrazine treatment and yielded, respectively, 0.07 g. of phenylhydrazid,

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melting interval 200–204°, and 0.12 g. of phenylhydrazid, melting interval 198–200°. The treatment of these 2 lots of phenylhydrazid is discussed under "The High Melting Phenylhydrazids" (see below). The non-crystalline hydrazids were discarded.

The 8.24 g. of gum $[\alpha]_D^{20} = -35°$, extremely soluble in ether, was examined for *d*-erythronic acid. This could not be proved present. A search for lactic acid showed none to be present. Glyceric acid was next sought for by conversion of the gum—now 7.46 g.—into the quinine salt.[1] The crude salt was crystallized from a small amount of water. There was thus obtained 3.00 g. of quinine salt insoluble in water, melting interval 175–178°, and 26.45 g. of quinine salt soluble in water.

Quinine Salt Insoluble in Water; Quinine *l*-Glycerate.—The salt was recrystallized from 30 cc. of absolute alcohol to free it from excess quinine. There was obtained 2.10 g. of crystals which were recrystallized from water and gave 1.17 g. of salt with the melting interval 178–180° and $[\alpha]_D^{20}$ —116.50°; *i. e.*, 1.0000 g. of crystals in 20 cc. aqueous solution gave α in a 1 dcm. tube —5.82°. Quinine *l*-glycerate prepared from Kahlbaum's calcium *dl*-glycerate was found to have a melting interval of 176–180° and $[\alpha]_D^{20}$ —116.90°. There is, therefore, no doubt that *l*-glyceric acid was present in the gum under discussion.

Quinine Salts Soluble in Water; a C_4-Saccharinic Acid.—The soluble quinine salts weighed 26.45 g. They were recrystallized from 3 parts of absolute alcohol and yielded a total of 8.49 g. of crystalline salt with melting interval 168–172°, $[\alpha]_D^{20}$ —120.30°. The mother liquor was discarded.

The 8.49 g. of crystalline quinine salt was hydrolyzed.[2] The ether-soluble gum finally obtained weighed 1.79; $[\alpha]_D^{20}$ —52.5°. A titration showed that 0.167 g. of this gum required 3.5 cc. of 0.1 *N* alkali to produce the first color in the indicator and that a total of 15.55 cc. was necessary for complete neutralization. This is almost exactly the theoretical amount for a C_4-saccharinic acid—$C_4H_8O_4$—calculated as 77.5% lactone.

The remaining gum (1.50 g.) was converted into the phenylhydrazid. Three crops of crystals were obtained: 0.65 gram, m. p., 102°; 0.55 g., melting interval 100–102°; and 0.30 g., melting interval 95–100°. These 3 crops of crystals were combined and recrystallized from 4 parts of absolute alcohol. There was thus obtained a crop of crystals, triangular plates with rounded corners, which weighed 1.15 g. They melted at

[1] The quinine salts of acid gums were made in precisely the same manner as the brucine salts except that the extractions to remove the excess quinine were made with ether instead of benzol.

[2] Quinine salts were hydrolyzed in precisely the same manner as brucine salts except that the aqueous filtrate from the precipitated quinine was extracted with ether instead of benzol.

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102.5° and had $[\alpha]_D^{20}$ —12.98°; *i. e.*, 0.7519 g. of substance in 25 cc. aqueous solution gave α in a 1 dcm. tube —0.39°.

That the gum now under discussion was a C_4-saccharinic acid and not a C_4-aldonic acid is, we think, established by analyses of the above mentioned 1.15 g. of phenylhydrazid.

	Calc. for C_4-sacc. phenylhydrazid, $C_{10}H_{14}N_2O_3$:	Calc. for C_4-aldonic phenylhydrazid, $C_{10}H_{14}N_2O_4$:	Found.		
			I.	II.	III.
C.....	57.14	53.1	56.80	57.00	...
H.....	6.72	6.20	6.85	6.88	...
N.....	13.34	12.39	...	...	13.64

There seems to us to be little doubt that this substance is the phenylhydrazid of a dioxybutyric acid. Unfortunately, it is at present impossible to identify it further; that is, to determine of which particular one of the 10 possible optically-active stereoisomeric dioxybutyric acids it is the phenylhydrazid. Work has been begun in this laboratory on the preparation of all the possible dioxybutyric acids with a view to identifying this phenylhydrazid as well as to the furnishing of information as to the properties and physical constants of these acids and their derivatives to be used in future work on the sugars.

The "preserved" part of the original oxidation gum soluble in ether also yielded this C_4-saccharinic phenylhydrazid. The following additional information was supplied by this material. The acid itself is extremely soluble in ether and has $[\alpha]_D^{20}$ —72.4°. The brucine salt has a melting point of 178° and $[\alpha]_D^{20}$ —23.60°.

The Non-crystalline Brucine Salt; Calcium Glycollate.—This salt weighed 60.33 g. It was hydrolyzed and yielded 10.90 g. of gum. This gum was converted into calcium salts. The crude calcium salts were crystallized from water and yielded 5.03 g. of crystals. That these were crystals of calcium glycollate was proved by the following analysis: A portion of the air-dried salt, 0.5504 g., was heated at 110° to constant weight and left a residue of 0.3954 g. of anhydrous salt. This anhydrous salt was ignited to constant weight and left a residue of 0.1160 g. of calcium oxide.

Calc. for $Ca(C_2H_3O_3)_2.4H_2O$: H_2O, 27.48; CaO, 29.47. Found: H_2O, 27.98; CaO, 29.33.

Attempts to identify the constituents of the non-crystalline calcium salts proved unsuccessful.

The Simple Acid Fraction Insoluble in Ether but Soluble in Ethyl Acetate.—This gum weighed 36 g. and had $[\alpha]_D^{20}$ about +15°. It was divided into 2 parts. The part used for the separation here described weighed 18 g. The gum was quite mobile. It was extracted with ether in which 9.75 g., $[\alpha]_D^{20}$ = +1.85°, dissolved. The insoluble part was then extracted with absolute alcohol. The residue from this extraction was

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discarded and the alcohol-soluble gum treated with phenylhydrazine. There was obtained a total of 3.22 g. crystalline phenylhydrazid melting interval 209–210°, which is discussed under "High Melting Hydrazids," and a quantity of non-crystalline phenylhydrazid which was hydrolyzed and gave 3.4 g. of gum with $[\alpha]_D^{20}$ +6.25°. This gum was reunited with the 9.75 g. of gum, $[\alpha]_D^{20}$ +1.85°, which made a total of 12.75 g. This gum was then converted into brucine salts. Recrystallization of the crude salts from 2 parts of absolute alcohol effected a separation into 26.40 g. crystalline brucine salts, melting interval 180–196°, and 25 g. of non-crystalline salts which have been preserved for future study.

The Crystalline Brucine Salts; Quinine *l*-Glycerate.—The 26.40 g. of brucine salts were hydrolyzed and gave 6.15 g. of very mobile gum. This gum was extracted with cold ether in which 4.65 g. gum, $[\alpha]_D^{20}$ —14°, dissolved. From the ether-insoluble part there was obtained 0.60 g. of phenylhydrazid, melting interval 205–206°, which is treated under "High Melting Phenylhydrazids."

The 4.65 g. of gum, $[\alpha]_D^{20}$ —14°, was converted into the quinine salt. There was obtained 11.50 g. of crude quinine salt which by recrystallization from 2 parts of absolute alcohol gave 2.1 g. of crystals. These crystals when recrystallized from water yielded a crop of 1.34 g. of salt with melting interval 179–180° and with $[\alpha]_D^{20}$ —116.20°; *i. e.*, 0.9346 g. of salt in 20 cc. of aqueous solution gave α in 1 dcm. tube —5.43°. This salt was undoubtedly quinine *l*-glycerate.

The High Melting Phenylhydrazids; *d*-Arabonic Phenylhydrazid.—The high melting phenylhydrazids had a total weight of 3.82 g. They had $[\alpha]_D^{20}$ —13.12°. They were recrystallized from 300 cc. of 95% alcohol. The crystals obtained weighed 2.84 g. and had a melting point of 214°, which is the recorded melting point for *d*-arabonic phenylhydrazid. Analysis gave the following results:

Calc. for $C_{11}H_8N_2O_4$: C, 51.56; H, 6.30; N, 10.94. Found: C, 51.50; H, 6.58; N, 10.97.

The substance was undoubtedly *d*-arabonic phenylhydrazid.

III. THE PREPARATION AND PROPERTIES OF MALTOBIONIC ACID.

This study of maltobionic acid and some of its derivatives was undertaken to provide information about the properties of glucosido acids, to be useful in the experiments just discussed. The method of oxidation described here, although practically a duplicate of that of Emil Fischer,[1] differs considerably from Fischer's procedure in detail.

Oxidation of Maltose to Maltobionic Acid.—Fifty g. of maltose hydrate was dissolved in 500 cc. of water. To this solution was added 8.5 cc. of bromine and 41.28 g. of lead carbonate. The flask was provided with

[1] *Ber.*, **22**, 1941 (1889).

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a reflux condenser and was vigorously shaken until the bromine had dissolved. The mixture was allowed to stand for 7 days at room temperature. The resulting pale yellow solution was separated from the precipitated lead bromide by filtration. A vigorous current of air was drawn through the filtrate to remove the excess bromine. This left a clear, colorless solution. To remove the bromide ion completely, a suspension of silver carbonate in water was added to the solution until it gave a faint test for silver. In order to remove the silver and lead completely from the filtered solution, the latter was saturated with hydrogen sulfide. After the sulfides of silver and lead had been separated by filtration, the filtrate was subjected to distillation *in vacuo* for a time to remove the hydrogen sulfide, whereupon the solution in the distilling flask was made up to 1000 cc. and aliquot portions used for tests. These tests showed that α of the solution was $+105°$; that 83% of the sugar had been oxidized, and that the acid was present as free acid to the extent of 78%.

The remaining solution, 950 cc., was heated at 60° for 10 hours with an excess of calcium carbonate. The crude calcium salt obtained was twice dissolved in one part of water and precipitated with 5 parts of absolute alcohol. There was thus obtained 40.90 g. of gummy calcium salt. To this was added a similar lot of calcium salt from a previous experiment. The combined salt, 81.1 g., was once more dissolved in one part of water, and precipitated with 5 parts of 95% alcohol. The precipitated salt was transferred to a mortar with small amounts of water, covered with absolute alcohol, and ground to a powder. A total of 67.70 g. of vacuum-dried calcium salt in the form of a powder, which was practically free from sugar, was finally obtained.

Analysis and Rotation of Calcium Maltobionate.—That this salt was pure calcium maltobionate was proved by an analysis. A portion of it, 0.5575 g., was ignited to constant weight in a platinum crucible and left a residue of 0.0413 g. of calcium oxide.

Calc. for $Ca_{12}(H_{21}O_{12})_2$: CaO, 7.42. Found: 7.41.

The salt in water solution was found to have $[\alpha]_D^{20}$ $+97.5°$, *i. e.*, 0.3386 g. of salt dissolved in 8.6672 g. of water gave α in a 1 dcm. tube 3.71°.

Maltobionic Acid.—The remaining 66.77 g. of calcium salt was dissolved in water and treated at 60° with 11.16 g. of oxalic acid. The filtrate from the calcium oxalate was made up to 1000 cc. This solution had $[\alpha]_D^{20}$ $+98.3°$ calculated on the basis of its having contained 63.4 g. of maltobionic acid, *i. e.*, α in 1 dcm. tube $+6.23°$.

Further studies of portions of this solution gave the following information about maltobionic acid: It exists in water solution practically entirely as free acid; 15 cc. of the solution which contained 0.951 g. of acid required 24.6 cc. of 0.1 *N* alkali for the first appearance of color in phenol-

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phthalein and 26.6 cc. for complete neutralization. It exhibits slight tendency to form a lactone; after a portion of the solution had been subjected to complete distillation *in vacuo*, the residue heated *in vacuo* at 100° for 5 hours, dissolved in water and titrated quickly with 0.1 *N* alkali, the titration showed the acid to be present practically entirely as free acid. It does not reduce Fehling's solution. It is miscible with water in all proportions, is practically insoluble in absolute alcohol and in ethyl acetate and quite insoluble in boiling ether. It is not hydrolyzed by approximately 0.2 *N* sodium hydroxide; 10 cc. of the solution to which 7.09 cc. of 0.5 *N* sodium hydroxide had been added was heated for 10 hours on the boiling water bath under a reflux condenser, after which the resulting solution had a brown color, did not reduce Fehling's solution and had suffered almost no change in rotation. It is completely hydrolyzed by approximately 0.2 *N* sulfuric acid; to 9.51 g. of the acid gum was added 19.88 cc. of 0.5 *N* sulfuric acid and 30 cc. of water, the mixture was heated for 20 hours under a reflux condenser, the sulfuric acid was removed with barium hydroxide, and the filtrate from the barium sulfate treated with calcium carbonate. By this treatment there was obtained, finally, 4.30 g. of pure calcium gluconate and 3.60 g. of glucose, m. p. 149°.

The Brucine Salt of Maltobionic Acid.—The crude salt made in the usual way from 50 cc. of the solution and 3.48 g. of brucine could not be induced to crystallize. It was finally ground to a powder in a mortar in the presence of absolute alcohol and ether. The powder so obtained was dried *in vacuo* over sulfuric acid. A portion of it, 2.25 g., was dissolved in 1 cc. of water and 5 cc. of absolute alcohol. Crystals, 1.45 g., separated from the solution after long standing. The entire powder was transformed into crystals in the same manner. To obtain the pure salt, 4 g. of these crystals was dissolved in 4 cc. of water and 35 cc. of absolute alcohol. Crystals began to form in this solution at the end of 10 hours, but the salt had crystallized out completely only after having stood a week. In this way 2.85 g. of crystals was obtained. Dried to constant weight *in vacuo* over sulfuric acid, these melted at 153°. They had $[\alpha]_D^{20}$ +38.05°, *i. e.*, 0.4872 g. of salt dissolved in 9.869 g. of water gave α in a 1 dcm. tube +1.79°. This positive rotation of a brucine salt is unusual, if not, indeed, unique.

Other Derivatives of Maltobionic Acid.—The phenylhydrazid and strychnine, quinine and cinchonine salts of maltobionic acid were prepared. The crude products were in all cases gums. They could be ground to powders in a mortar in the presence of absolute alcohol; but these powders could not be recrystallized and became gummy in the presence of even traces of moisture.

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Summary.

TABLE I.—SUBSTANCES ACTUALLY ISOLATED FROM THE OXIDATION PRODUCTS OF MALTOSE, PER 100 G. OF MALTOSE HYDRATE.

	Maltose and H_2O_2. Grams.	Maltose and air. Grams.
Formic acid	43.30	8.94
Glucosido acids	37.0	15.56
d-Glucose	19.22	9.98
d-Erythronic lactone	1.40	0.32
d-Arabonic phenylhydrazid	2.96	1.94
Simple acids	13.0	63.06
Calcium glycollate	1.66	6.68
Calcium oxalate	0.14	...
Quinine *l*-glycerate	...	3.34
C_4-Saccharinic phenylhydrazid	...	1.54
Calcium *d*-arabonate	1.16	...
d-Arabonic phenylhydrazid	...	3.78

A study of the preparation and properties of maltobionic acid, its calcium, brucine, strychnine, quinine and cinchonine salts and its phenylhydrazid is also reported.

CHICAGO, ILLINOIS.

[CONTRIBUTION FROM THE CARBOHYDRATE LABORATORY, BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

THE ISOMERIC TETRACETATES OF *l*-ARABINOSE AND BETA-TRIACETYL-METHYL-*l*-ARABINOSIDE.

BY C. S. HUDSON AND J. K. DALE.

Received March 25, 1918.

The possibility of the existence of 2 isomeric tetracetates of arabinose has been foreshadowed by the preparation of an isomeric pair of completely acetylated derivatives of most of the other naturally occurring mono- and disaccharides. Stone[1] acetylated arabinose by heating it with acetic anhydride and sodium acetate for one hour at 105°, but he obtained only a sirup. By shaking a solution of bromoacetyl-arabinose in acetic acid with silver carbonate, Chavanne[2] obtained crystals melting at 80° which he supposed were tetracetyl-arabinose but the quantity was too small for analysis.

Although the form of arabinose tetracetate that can be obtained directly by the acetylation of arabinose crystallizes readily when nearly pure, its preparation caused us great difficulty because there was formed at the same time a large proportion of sirupy material which interfered with its crystallization. With the aid of crystals that were produced by the method of Chavanne, the sirups that resulted from the acetylation of ara-

[1] *Am. Chem. J.*, 15, 653 (1893).

[2] *Compt. rend.*, 134, 661 (1902).

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binose with acetic anhydride and sodium acetate could be brought to crystallization but even under the best conditions the yield was small. The pure compound, which will be named *α-l-arabinose tetracetate*, had a specific rotation in chloroform of +42.5°. When a solution of it in acetic anhydride containing a little zinc chloride was warmed on the steam bath the specific rotation gradually increased and became constant about 70° higher than the initial value. From this transformed solution a second crystalline tetracetate of arabinose was obtained, having a specific rotation in chloroform of +147.2°. It will be designated *β-l-arabinose tetracetate*. This naming of the two isomers is in accordance with the fact that they are derivatives of the *l*-form of arabinose, and hence the one of more positive specific rotation is named beta.[1]

It has been shown in previous articles[2] that considerations of molecular structure lead to the conclusion that the difference in molecular rotation between the α- and β-forms of the fully acetylated aldose sugars should be equal. The experimental evidence in support of this relationship is collected in the accompanying table which includes the molecular rotations in chloroform at 20° of all the previously described pairs of completely acetylated aldose sugars with the addition of those of the arabinose tetracetates that are described in this article.

Substance.	Molecular rotation of α-form.	Molecular rotation of β-form.	Difference.
d-Glucose pentacetate	+39,600	+ 1,500	+38,100
d-Lactose octacetate	+36,500	— 2,900	+39,400
d-Maltose octacetate	+83,000	+42,500	+40,500
d-Cellose octacetate	+27,800	—10,200	+38,000
d-Glucosamine pentacetate	+36,400	+ 470	+35,930
d-Chondrosamine pentacetate[3]	+39,500	+ 4,100	+35,400
d-Gentiobiose octacetate	+35,500	— 3,600	+39,100
d-α-Glucoheptose hexacetate	+40,200	+ 2,200	+38,000
d-Mannose pentacetate	+21,400	— 9,800	+31,200
d-Galactose pentacetate	+41,600	+ 8,900	+32,700
d-Xylose tetracetate	+28,300	— 7,900	+36,200
l-Arabinose tetracetate	+13,400	+46,800	—33,400[4]

[1] Hudson, THIS JOURNAL, 31, 66 (1909).

[2] THIS JOURNAL, 37, 1270, 1276, 1280, 2748 (1915); 38, 1431, 1575 (1916); 39, 1272 (1917); *J. Ind. Eng. Chem.*, 8, 379 (1916).

[3] Since Levene (*J. Biol. Chem.*, 31, 609 (1917)) has shown that chondrosamine belongs in the *d*-series of sugars, he having synthesized it from *d*-xylose, the naming of its α- and β-pentacetates must be changed from that which we used in a former article (THIS JOURNAL, 38, 1431 (1916)) and the more levorotatory form designated as beta.

[4] The negative sign of this value follows from the system of nomenclature of α- and β-forms because the sugar belongs to the *l*-series. The difference for *d*-arabinose tetracetates would be +33,400, conforming in sign to the values for the other *d*-sugars of the table.

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Experimental.

Preparation of Bromoacetyl-*l*-arabinose.—Chavanne[1] has prepared bromoacetyl-arabinose by the action of acetyl bromide upon the sugar. One of us[2] has prepared the bromoacetyl derivatives of a number of the sugars by the action of a saturated solution of hydrobromic acid in acetic anhydride in place of acetyl bromide. This method was also found applicable for the preparation of bromoacetyl-arabinose. Twenty-five g. of finely powdered *l*-arabinose was treated in an Erlenmeyer flask at room temperature with 150 cc. of a saturated solution of hydrobromic acid in acetic anhydride. A vigorous reaction followed. The resulting straw-colored sirup was cooled, mixed with 400 cc. of chloroform and the solution shaken with ice water, sodium bicarbonate solution and again with ice water. After drying with calcium chloride the solution was evaporated under diminished pressure to a thick sirup, which crystallized in the flask. The crystals were washed out of the flask with a little ether, dried on a Büchner funnel and then recrystallized from ether. Eight g. of the pure compound was obtained.

Conversion of Bromoacetyl-*l*-arabinose into α-Tetracetyl-*l*-arabinose.—Eight g. of pure bromoacetyl-*l*-arabinose was dissolved in 200 cc. of glacial acetic acid and shaken with 10 g. of silver acetate until a few drops gave no test for halogen with silver nitrate. The silver salt was then filtered off and the filtrate was diluted with water, neutralized with sodium bicarbonate and extracted with an equal volume of chloroform. The chloroform extract was dried with calcium chloride and evaporated to a thick sirup which was then dissolved out of the flask with a little warm ether. This solution on evaporation in a current of air deposited beautiful plate-like crystals. After filtering and washing on a Büchner funnel 4.0 g. was obtained. The melting point of this product was 94 to 96° and the specific rotation in chloroform $[\alpha]_D^{23} = +45.4°$, values which are very near the ones found for pure α-tetracetyl-*l*-arabinose, now to be described.

Preparation of α-Tetracetyl-*l*-arabinose by Direct Acetylation of *l*-Arabinose.—To a boiling solution of 5 g. of anhydrous sodium acetate in 40 cc. of acetic anhydride 10 g. of *l*-arabinose was gradually added, and the solution was boiled a few minutes, cooled and poured into about 800 cc. of cold water. A sirup immediately separated and settled to the bottom of the flask. The supernatant acid liquid was poured off and the sirup washed with a little cold water, after which it was dissolved in a small amount of alcohol, decolorized with carbon and then evaporated to a thick sirup. This sirup was seeded with tetracetate crystals obtained as previously described from the bromoacetyl compound and after a few days it had partially crystallized. The crystalline material was easily separated from

[1] *Compt. rend.*, **134**, 661 (1902).

[2] Dale, THIS JOURNAL, **37**, 2745 (1915); **38**, 2187 (1916).

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the large amount of sirupy mother liquor by thinning out with ether and filtering on a Büchner funnel. A small amount of the same substance was also crystallized from the acid solution which had been decanted from the original sirupy material. It was neutralized with sodium bicarbonate, filtered and extracted with chloroform. The extract was dried with calcium chloride and evaporated to a thick sirup, which slowly deposited crystals of arabinose tetracetate. From 50 g. of arabinose there was obtained by this method 11.0 g. of the nearly pure tetracetate. It was recrystallized from water until its specific rotation became constant. The melting point of the pure substance, *α-tetracetyl-l-arabinose*, was 97° (corr.).

A solution consisting of 0.6679 g. of the tetracetate made up to 25 cc. with chloroform (*Chloroformum purificatum*, U. S. P.) rotated 2.27 circular degrees to the right in a 200 mm. tube, using sodium light, hence $[\alpha]_D^{22} = +42.5°$.

Acetyl determinations, made by boiling in a quartz flask with a reflux condenser 0.3 g. substance with 100 cc. 0.1 *N* H_2SO_4 during 4 hours, gave 75.80 and 75.65% acetic acid, which agree with the theoretical value for arabinose tetracetate, 75.48%.

Calc. for $C_{13}H_{18}O_9$: C, 49.03; H, 5.70. Found: C, 48.86; H, 5.74.

Transformation of α-Tetracetyl-*l*-arabinose to the Isomeric β-Form.—Twelve g. of *α-l*-arabinose tetracetate was dissolved in 25 cc. of acetic anhydride containing one g. of zinc chloride and the solution heated on the steam bath until the specific rotation reached a constant value, which was found to be about 70° higher than the initial reading. When this solution was poured into 700 cc. of ice water an insoluble phase separated and soon crystallized. The yield was 2 g. The filtrate from this crystalline material was neutralized with sodium bicarbonate and extracted with chloroform. The extract was dried with calcium chloride and evaporated to a thick sirup, which crystallized after being stirred with successive portions of cold water and the crystals were recrystallized once from water with a yield of 2 g. These two products had nearly the same specific rotation and melting point. By this method 12 g. of this substance was prepared and it was found to be a tetracetate of arabinose, isomeric with the arabinose tetracetate which from it was prepared. It was purified by recrystallization from water until its specific rotation became constant. The pure substance melted at 86° (corr.). Since it is more dextrorotary than its isomer it is to be named *β-tetracetyl-l-arabinose*, its isomer of m. p. 97° being the *α*-form.

A chloroform solution (*Chloroformum purificatum*, U. S. P.) containing 1.2047 g. of the substance in 25 cc. solution rotated to the right, 14.19 circular degrees, in a 200 mm. tube, using sodium light, hence $[\alpha]_D^{21} = +147.2°$.

Acetyl determinations made by boiling in a quartz flask with a reflux condenser 0.3 g. substance with 100 cc. 0.1 *N* H_2SO_4 during 4 hours gave 75.57 and 75.34% acetic acid, which agree with the theoretical value for arabinose tetracetate, 75.48%.

Calc. for $C_{13}H_{18}O_9$: C, 49.03; H, 5.70. Found: C, 48.98; H, 5.76.

Preparation of β-Triacetyl-methyl-*l*-arabinoside.—It had been hoped

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that both the α- and β-forms of triacetylmethyl-arabinoside might be prepared in a crystalline form, but though the β-form crystallized readily all attempts so far to obtain the α-form in a crystalline state have failed. By shaking bromoacetyl-*l*-arabinose with methyl alcohol and silver carbonate and also by acetylating α-methyl-*l*-arabinoside with acetic anhydride and sodium acetate only clear, colorless sirups have been obtained. When β-methyl-*l*-arabinoside was acetylated the product crystallized almost immediately.

Four g. of fused sodium acetate was dissolved in 40 cc. of boiling acetic anhydride and to this solution was gradually added 10 g. of β-methyl-*l*-arabinoside, of m. p. 170° and $[\alpha]_D^{20} = +246°$. The solution was then boiled 2 or 3 minutes, cooled and poured into 800 cc. of cold water. A sirupy phase separated which on stirring soon crystallized. After recrystallization from water there was obtained 11 g. with $[\alpha]_D^{22} = +182.2°$. Another recrystallization from water was made.

A chloroform (*Chloroformum purificatum*, U. S. P.) solution containing 1.1042 g. substance in 25 cc. solution rotated 16.08 circular degrees to the right in a 200 mm. tube, using sodium light, hence $[\alpha]_D^{23} = +182.0$. The melting point of the pure substance, *β-triacetylmethyl-l-arabinoside*, was 85° (corr.).

Acetyl determinations made by shaking 0.30 g. of the compound with 75 cc. 0.1 *N* NaOH in glass stoppered bottles for 2 and 4 hours gave, respectively, 61.60% and 62.40% acetic acid. Calc. for triacetylmethyl-*l*-arabinoside, 62.07%.

Calc. for $C_{12}H_{18}O_8$: C, 49.63; H, 6.25. Found: C, 49.50; H, 6.35.

In determining whether the crystalline compound just described is the α- or β-isomer, the fact that it was made by direct acetylation of β-methyl-*l*-arabinoside, so named because it is more dextrorotary than α-methyl-*l*-arabinoside, is good evidence for the β-classification. In addition we have the data at hand for a calculation of the rotations of both the α- and β-forms of triacetylmethyl-*l*-arabinoside; it will be seen that the measured specific rotation of the compound that is under investigation, though not agreeing exactly with the calculated value for the β-form, is close enough to it to fully warrant classification in the β-series.

The molecular rotations of the α- and β-triacetylmethyl-*l*-arabinosides may be denoted by $(-A - B)$ and $(A - B)$,[1] respectively, when A denotes the rotation due to the terminal asymmetrical carbon atom and $-B$ that due to the remainder of the structure. The difference between these 2 molecular rotations is $-2A$. Using similar notation the difference between the molecular rotations of the α- and β-tetracetyl-methyl-*d*-glucosides is $2A$, and it has been shown in the last article cited that this value is $+53{,}900$, hence $A = 26{,}950$. A value for B can be obtained from the measured molecular rotations of the α- and β-forms of tetraacetyl-*l*-arabinose. Since these compounds differ in structure from the acetylated

[1] For explanation of these terms see THIS JOURNAL, 31, 66 (1909); 37, 1264 (1915).

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methyl arabinosides only in respect to the terminal asymmetric carbon atom which has an acetyl instead of a methyl group, the rotation of the 2 forms of the tetracetate may be expressed as $(-A' - B)$ and $(A' - B)$, and their sum, $-2B$, from the values of the molecular rotations of the α- and β-arabinose tetracetates given earlier in this article, is +60,200 or $-B$ = 30,100. Hence, the specific rotation of α-triacetyl-methyl-*l*-arabinoside (M. W. 290) is calculated to be $(-A - B)/290$ = (—26,950 + 30,100)/290 = +11°, and that of the β-form (26,950 + 30,100)/290 = +197°. The calculated value for the β-form, +197°, is near enough to the specific rotation (+182°) of the triacetyl-methyl-*l*-arabinoside that we have described to justify its classification in the β-series.

WASHINGTON, D. C.

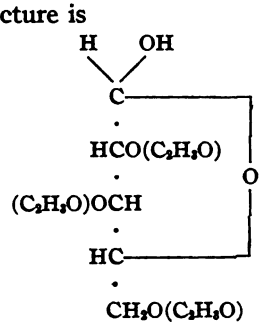
[CONTRIBUTION FROM THE CARBOHYDRATE LABORATORY, BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

TRIACETYL-*d*-XYLOSE AND ALPHA TRIACETYLMETHYL-*d*-XYLOSIDE.

BY C. S. HUDSON AND J. K. DALE.

Received March 28, 1918.

In a recent article one of the authors[1] described the preparation from *d*-xylose ($[\alpha]_D$ = +19°) of bromoacetyl-*d*-xylose, a crystalline compound which was found to be very similar in its reactions to bromoacetyl-glucose. The bromine atom could be replaced by an oxymethyl or an oxyacetyl group by reactions that are quite analogous to those by which tetracetyl-methyl-glucoside and pentacetyl-glucose are prepared from bromoacetyl-glucose. An incompletely acetylated derivative of glucose, tetracetyl-glucose, can also be prepared from bromoacetyl-glucose by the substitution of an hydroxyl group in place of the bromine atom.[2] In analogy with this reaction a partially acetylated derivative of xylose, *triacetyl-d-xylose*, has been prepared from bromoacetyl-xylose. On the assumption that it is a γ-cyclo derivative its structure is



This triacetate showed mutarotation in both chloroform and water

[1] Dale, THIS JOURNAL, 37, 2745 (1915).

[2] Fischer and Kurt, *Ber.*, 45, 912 (1912).

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solution. In the former the specific rotation changed from an initial value of $[\alpha]_D^{23} = +70.11°$ to a constant value of $[\alpha]_D^{21} = +40.8°$ in about 10 days, the temperature being 20°. The mutarotation of the substance is to be expected because tetracetyl-glucose exhibits mutarotation; in both cases the mobility of the H and OH groups on the end asymmetric carbon atom can give rise to α- and β-forms which can establish an equilibrium in solution. The direction of the mutarotation indicates that the crystalline form of triacetyl-*d*-xylose that we have had in hand belongs to the α-series. It is true that by the acetylation of this triacetate the β-form of tetracetyl-xylose has been isolated as crystals (see below), but this fact does not alter the conclusion because the triacetate doubtless mutarotates very rapidly in hot acetic anhydride containing sodium acetate and thus yields the β-tetracetate, just as both α- and β-glucose yield β-glucose pentacetate by this method of acetylation.[1]

Optical Superposition among the Acetylated Derivatives of Xylose.—From a comparison of the molecular structures of the α- and β-pentacetates of glucose and the α- and β-tetracetyl-methyl-glucosides the authors[2] drew the conclusion that the sum of the molecular rotations of the two pentacetates is presumably equal to the sum of the molecular rotations of the 2 tetracetyl-methyl-glucosides, and this deduction was well verified by measurements of the specific rotations of the 4 compounds. A similar relation exists between the molecular structures of the α- and β-tetracetates of xylose and the α- and β-triacetylmethyl-xylosides, hence, it is to be expected that the sum of the molecular rotations of the α- and β-tetracetates of xylose is equal to that of the α- and β-triacetyl-methyl-xylosides. The preparation and properties of α-triacetyl-methyl-xyloside are described below, those of the other 3 compounds having been recorded in previous contributions[3] from this laboratory. In Table I are recorded the specific and molecular rotations of these compounds in chloroform (U. S. P.) solution, while in the last column the sums of the molecular rotations of the 2 pairs are shown.

TABLE I.

Compound.	Specific rotation.	Molecular rotation.	Sum of molecular rotation of each pair.
α-Xylose tetracetate	+ 89.1	+28,300	+20,400
β-Xylose tetracetate	— 24.9	— 7,900	
α-Triacetyl-methyl-xyloside	+119.6	+34,700	+17,100
β-Triacetyl-methyl-xyloside	— 60.7	—17,600	

The agreement is not so good as it was in the case of the similar derivatives of glucose.

[1] Hudson, *J. Ind. Eng. Chem.*, **8**, 379 (1916).
[2] THIS JOURNAL, **37**, 1264 (1915).
[3] Dale, *Ibid.*, **37**, 2745 (1915); Hudson and Johnson, *Ibid.*, **37**, 2748 (1915).

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A comparison can also be made between the 2 triacetyl-methyl-xylosides, the corresponding 2 tetracetyl-methyl-glucosides and the tetracetyl-methyl-galactosides. If $(A + B)$[1] represents the molecular rotation of α-triacetyl-methyl-xyloside where A is the rotation of the end asymmetric carbon atom and B that of the remainder of the molecule, the molecular rotation of β-triacetyl-methyl-xyloside may be represented by $(-A + B)$. In similar manner let $(A + B')$ and $(-A + B')$ represent the molecular rotations of the α- and β-tetracetyl-methyl-glucosides and $(A + B'')$ and $(-A + B'')$ those of the α- and β-tetracetyl-methyl-galactosides. The difference between the rotations of each of these pairs is the same quantity, $2A$. This conclusion is tested in Table II, the rotations referring to chloroform (U. S. P.) solutions.

TABLE II.

Compound.	Specific rotation.	Molecular rotation.	Difference of molecular rotation for each pair ($2A$).
α-Triacetyl-methyl-*d*-xyloside	+119.6	+34,700	+52,300
β-Triacetyl-methyl-*d*-xyloside	— 60.7	—17,600	
α-Tetracetyl-methyl-*d*-glucoside	+130.5	+47,300	+53,900
β-Tetracetyl-methyl-*d*-glucoside	— 18.3	— 6,600	
α-Tetracetyl-methyl-*d*-galactoside	+133.0	+48,400	+53,100
β-Tetracetyl-methyl-*d*-galactoside	— 13.0	— 4,700	

The agreement of the values in the last column is satisfactory. Since the acetylated xylosides thus fit in with the similar derivatives of two other sugars, it seems probable that the lack of better agreement between the two sums in Table I is referable to some abnormal condition affecting the tetracetates of xylose, or one of them.

Experimental.

Preparation of Triacetyl-*d*-xylose.—Twenty g. of bromoacetyl-xylose was dissolved in 60 cc. of acetone to which had been added 2 cc. of water, and the solution was shaken with freshly prepared silver carbonate until carbon dioxide ceased to be evolved and a few drops showed no reaction for halogen with silver nitrate. After the mixture of silver carbonate and silver bromide had been filtered off, the filtrate was evaporated to a sirup which slowly deposited crystals on standing. The mixture of crystals and sirup was thinned with ether and the crystals separated by filtering on a Büchner funnel. The yield of this product after one recrystallization from ether was between 2 and 3 g. A total quantity of about 10 g. was prepared by this method. Triacetyl-*d*-xylose is easily soluble in chloroform and in acetone, somewhat soluble in water and in alcohol and only slightly soluble in ether. It readily reduces Fehling's solution on warming. The pure compound melted gradually at 138–141° (corr.).

Calc. for $C_{11}H_{16}O_8$: C, 47.8; H, 5.84. Found: C, 47.80; H, 5.93.

[1] THIS JOURNAL, 31, 66 (1909).

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Two acetyl determinations made by boiling 0.30 g. in a quartz flask with a reflux condenser with 50 cc. 0.25 *N* sulfuric acid for 2 and 3 hours, respectively, gave 65.17% and 64.99% acetic acid, which results agree with the theoretical value for triacetyl-xylose, 65.22%.

After several recrystallizations from ether, 0.4540 g. of the substance made up to 25 cc. solution with chloroform (*Chloroformum purificatum*, U. S. P.) showed an initial reading to the right of 2.56 circular degrees in a 2 dcm. tube, using sodium light, hence $[\alpha]_D^{21} = +70.45°$. After another recrystallization from ether a duplicate measurement in which 0.8041 g. of the compound were used gave as the initial specific rotation $[\alpha]_D^{23} = +70.11°$. As mentioned before, the reading slowly changed from this value to become constant in about 10 days at +40.8°.

β-Tetracetyl-*d*-xylose from Triacetyl-*d*-xylose.—Two g. of triacetyl-*d*-xylose was acetylated by boiling with 10 cc. of acetic anhydride and 0.5 g. of anhydrous sodium acetate. The solution was poured into water and the insoluble phase which at first separated as a thick sirup soon hardened into a crystalline mass. The crystals were filtered off and twice recrystallized from alcohol. There was obtained of the purified material 0.6 g. Its melting point was 126–128° (corr.), and its specific rotation in chloroform (U. S. P.) solution was $[\alpha]_D^{21} = -24.4°$. This melting point and specific rotation agree with those of β-tetracetyl-*d*-xylose.[1]

Preparation of α-Triacetylmethyl-*d*-xyloside.—To a boiling solution of 5 g. of anhydrous sodium acetate in 100 cc. of acetic anhydride 25 g. of α-methyl-*d*-xyloside was gradually added. The boiling was continued 2 or 3 minutes, the reaction mixture was then poured into about 800 cc. of cold water, and an insoluble sirup separated and soon crystallized. This was filtered off and recrystallized from alcohol. The yield was 19 g. It was further recrystallized from alcohol several times until its specific rotation became constant.

The pure substance melted at 86° (corr.). In chloroform (U. S. P.) solution 1.0116 g. of the compound in 25 cc. of the solution gave a reading to the right, 9.67° in a 2 dcm. tube, with sodium light, hence $[\alpha]_D^{20} = +119.5°$. After another recrystallization a similar measurement gave a specific rotation of $[\alpha]_D^{20} = +119.6°$.

Two acetyl determinations made by shaking 0.3 g. of the compound with 100 cc. 0.1 *N* sodium hydroxide for 2 and 4 hours, respectively, in glass stoppered bottles, at 0°, gave 62.08% and 62.12% acetic acid, which agree with the theoretical value for triacetyl-methyl-xyloside, 62.07%.

Calc. for $C_{12}H_{17}O_8$: C, 49.63; H, 6.25. Found: C, 49.40; H, 6.28.

Preparation of β-Triacetyl-methyl-*d*-xyloside by Direct Acetylation.—By the action of a solution of silver nitrate in 80% methyl alcohol upon bromoacetyl-xylose, one of the authors[2] has prepared β-triacetyl-methyl-*d*-xyloside. We have also succeeded in preparing it by acetylating β-

[1] Hudson and Johnson, THIS JOURNAL, 37, 2748 (1915).

[2] Dale, *Loc. cit.*

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methyl-*d*-xyloside. Fifteen g. of this substance was gradually added to a boiling solution of 6 g. of anhydrous sodium acetate in about 60 cc. acetic anhydride. After boiling for a few minutes the reaction mixture was cooled, mixed with 800 cc. of cold water, and an insoluble sirupy phase separated and crystallized almost immediately. After one recrystallization of the substance from water its specific rotation was found to be $[\alpha]_D^{22} = -60.9°$, and the melting point 115° (uncorr.). These values, which remained the same after another recrystallization, agree with those previously found for β-triacetyl-methyl-*d*-xyloside that had been prepared from bromo-acetyl-xylose.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE LABORATORIES OF AGRICULTURAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN.]

BY-PRODUCTS OF THE FERMENTATION OF CABBAGE.

BY V. E. NELSON AND A. J. BECK.

Received April 1, 1918.

The results of this investigation are merely the outgrowth of some work which was planned in this laboratory to shed further light upon the chemical changes taking place in silage and the direct cause of these transformations.

In the fermentation of green plant tissue two dominant factors contribute to the production of the various chemical by-products, namely enzymes and bacteria. To what extent enzymes are a factor to the exclusion of bacteria is a very debatable question requiring considerable experimental investigation before a solution can be made, and one which our experiments were planned to answer. For certain specific reasons we chose the cabbage instead of the corn plant as a method of solving this problem. Before any progress could be made, it was necessary to determine the by-products resulting from the fermentation of cabbage or sauerkraut, as it is commonly called.

As far as the authors are aware no systematic quantitative study of this product has been made.

Experimental.

For the estimation of acids, alcohols and esters of fermented products, certain methods were employed which have been little utilized by biological chemists. A detailed description of the methods will not be given here as it is the intention of one of the authors to discuss these methods in a forthcoming paper on the volatile by-products of certain soft cheeses, and a determination of the volatile fatty acids, esters and alcohols resulting from the growth of certain microörganisms on synthetic media. However, a very brief summary may not be out of place. For information more in detail, it is necessary to consult Suzuki, Hastings and Hart[1] on the volatile

[1] *J. Biol. Chem.*, 7, 431–458 (1910).

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by-products of cheddar cheese, Hart and Willaman[1] of this station and Dox and Neidig[2] on the by-products of corn silage; DuClaux's[3] original article in which the principles of the method are given in detail, and the work of Richmond,[4] who verified the findings of DuClaux.

Recently certain criticisms regarding the value of this method have been published. Of particular interest, mention is made of the work of Upson, Plum and Scott[5] of Nebraska, who condemned the method because of its failure of absolutely quantitative accuracy. This paper was completed before the above work appeared, and so we will not offer any data here to refute the claims set forth by these investigators. Richmond,[6] Suzuki,[6] and Lamb[7] have verified the findings of DuClaux, and work at this station has substantiated his data. It must be borne in mind that none of these investigators hold the DuClaux method to be as accurate as a standard analytical operation, but that it does yield fairly accurate quantitative results as measured in terms of biological chemical determinations. The recent work of Gillespie and Walters[8] confirms our viewpoint and substantiates data obtained at this station.

The Determination of Acids, Alcohols and Esters.

Cans of fermented cabbage were purchased on the market, the contents removed and finely comminuted by passing the material through a meat grinder. Five hundred g. was placed in a five-liter round-bottomed long-necked flask made slightly acid to congo red with sulfuric acid, and subjected to steam distillation until 2 liters was collected. The contents of the flask was kept in a pail of boiling water during the distillation so as to prevent condensation as much as possible. The volatile acids of the distillate were then titrated with 0.1 *N* barium hydroxide using phenolphthalein as an indicator and the alcohols and esters distilled from the barium salts of the acids. The alcohols and esters were repeatedly redistilled until 50 cc. was obtained. In each case two-thirds of the original distillate was collected until the required 50 cc. resulted. This latter solution, which is called the flavor solution, was saponified with 10 cc. of 20% potassium hydroxide and the alcohols distilled off. The acids which formerly were in ester combination are now in the form of potassium salts. The alcohols were concentrated by repeated distillations to 50 cc., and oxidized on the water bath by a solution of potassium dichromate in sulfuric acid, prepared

[1] THIS JOURNAL, 36, 1619–1625 (1914).
[2] *Res. Bull.* 7, Iowa Agr. Expt. Sta.
[3] *Traite de Microbiol.*, 3, 388 (1900).
[4] *Analyst*, 33, 305–313 (1908).
[5] THIS JOURNAL, 39, 731–742 (1917).
[6] *Loc. cit.*
[7] THIS JOURNAL, 39, 746–7 (1917).
[8] *Ibid.*, 39, 2027–2055 (1917).

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from 10 g. of potassium dichromate and 20 g. of strong sulfuric acid diluted with sufficient distilled carbon dioxide-free water to make 100 cc.

Finally the acids resulting from the oxidation of the alcohols were distilled from the oxidation mixture, and converted into barium salts by titrating with 0.1 *N* barium hydroxide. The potassium salts of the acids in ester combination were decomposed with dil. sulfuric acid, distilled and the distillate titrated with 0.1 *N* barium hydroxide solution. The free acids, and the acids resulting from the saponification of the esters and the oxidation of the alcohols were then subjected to the DuClaux method for analysis and estimation. Reference must be made to the original article for details concerning this process. In case the titer with 0.1 *N* barium hydroxide did not reach at least 5 cc., no attempt at differentiation was made.

TABLE I.—RESULTS OF ANALYSES.

Sample. No.	Dry matter. %.	Total acidity in cc. 0.1 *N* H_2SO_4 for 200 g. sample.	Total volatile acidity in 0.1 *N* H_2SO_4 for 200 g. sample.	Volatile acidity in cc.		
				0.1 *N* formic.	0.1 *N* acetic.	0.1 *N* propionic.
I.....	7.53	312.8	86.81	None	81.25	5.56
II.....	8.39	292.92	111.63	13.73	94.13	3.77
III.....	8.27	317.00	103.18	None	95.62	7.56
IV.....	8.27	317.00	109.88	None	101.94	7.94
V.....	5.05	176.32	85.95	None	51.27	34.68
VI.....	8.53	362.00	101.30	2.49	94.01	4.80
VII.....	7.47	190.00	91.19	None	83.74	7.45

Sample No.	Total volatile alcohols in cc. 0.1 *N* H_2SO_4.	Acids from alcohols in cc.		Acids in ester combination in cc. 0.1 *N* H_2SO_4.
		0.1 *N* acetic.	0.1 *N* propionic.	
I.....	86.81	81.25	5.56	1.1
II.....	Alcohols lost		..	Not determined
III.....	61.03	54.08	6.95	0.8
IV.....	61.28	56.33	4.95	0.52
V.....	105.14	95.24	9.9	Not determined
VI.....	Alcohols lost		..	1.7
VII.....	Alcohols lost		..	Lost

The results of 7 analyses are given in the table. It will be noted that the volatile acidity bears a considerable relation to the total acidity. Due to the fact that the quantitative methods for isolating lactic acid are very inadequate, it is difficult to say whether the total acidity minus the volatile acidity represents this component entirely. No succinic acid was found, and the lactic acid isolated was inactive.

Only 2 acids compose the volatile portion, namely acetic and propionic although, in 2 instances, formic acid was isolated. Acetic acid is present in the greatest quantity. No butyric or higher acids could be found. The alcohols are present in considerable amount, in fact, to the same extent as the volatile acids, and are comprised entirely of ethyl and propyl alcohols, the former being by far the most abundant.

The determination of the esters is very unsatisfactory for in the process

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incident to the estimation of these substances hydrolysis destroys by far the larger proportion. For that reason they were obtained only in small amounts, and yet they contribute largely to the flavor and aroma of the original product, as is evidenced by the fact that after saponification the characteristic flavor and aroma have disappeared.

In the 5 samples analyzed for methyl alcohol, which according to Hart and Willaman[1] and Hart and Lamb[2] is a natural constituent of corn silage, none was found.

In the extraction of the material under investigation by means of boiling ethyl alcohol for the isolation of the fixed acids, it was found that on concentrating and cooling, snow white, needle-shaped crystals separated, which had a melting point corresponding to 169°. After considerable time devoted in the identification of this substance, it was found to consist of pure mannitol. A careful review of the literature developed that mannitol had been detected in fermented cabbage by Feder.[3] In the 3 samples investigated by the authors, 1.9, 2.0, and 2.5%, respectively, was found.

Our method consisted in extracting with hot alcohol, cooling and allowing the material to crystallize from 95% alcohol, which it invariably did after a time varying from a few hours to a day or more.

Thinking that the mannitol might be a natural constituent of cabbage we undertook an examination of this material. Since mannitol has been found in a number of naturally occurring food products and higher plants, including turnip, celery, onion, carrot, pineapple, June grass, etc., it was not out of the range of possibility that the mannitol had its origin in the cabbage plant. However, we found such is not the case, for no mannitol could be isolated from cabbage, and consequently, must have resulted from bacterial decomposition of carbohydrates.

Conclusions.

The volatile acidity of fermented cabbage represents a considerable proportion of the total acidity.

Since no succinic acid or acid other than lactic was isolated from the fixed portion, the fixed acidity is concluded to be this component and in an inactive form.

Acetic and propionic acids comprise the volatile portion, although in 2 cases formic was isolated. Acetic acid is present in the greatest quantity. No butyric or higher acids were present.

Alcohols are found to the same extent as volatile acids and consist entirely of ethyl and propyl alcohols. No methyl alcohol was found.

The esters though present in small amount contribute an essential part in the flavor and aroma.

[1] *Loc. cit.*

[2] THIS JOURNAL, 36, 2114 (1914).

[3] *Z. Nahr. Genussm.*, 22, 295–6.

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Mannitol was isolated from fermented cabbage to the extent of 2.0 to 2.5%.

Since no mannitol was obtained from the natural plant, that found in the fermented product must have had its origin in the bacterial decomposition of carbohydrates.

[CONTRIBUTION FROM THE CARBOHYDRATE LABORATORY, BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

METHYLTETRONIC ACID AND ITS AMIDE.

BY C. S. HUDSON AND L. H. CHERNOFF.

Received April 10, 1918.

Methyltetronic acid has been previously prepared by Ruff and Kohn[1] who obtained it in the form of its lactone through the oxidation of methyltetrose with bromine. Methyltetrose, however, is difficult to make. We have obtained this lactone very easily by a simple method recently described by Nef, Hedenburg and Glattfeld[2] for the oxidation of arabinose and xylose. By passing a current of air through dilute solutions of these pentoses, they obtained *l*-erythronic lactone from *l*-arabinose and *d*-threonic lactone from *d*-xylose. Applying this method to rhamnose one would expect that its oxidation should yield methyltetronic lactone, and this proves to be the fact. Our yield of lactone was 9.6% of the theoretical. This is considerably more than Ruff and Kohn obtained (2%), and as the method which we have followed is much more direct and simple than theirs, it is recommended for the preparation of this lactone.

The configuration of rhamnose has been established[3] to be that of a methylpentose,

$$\begin{array}{c} \text{OH OH H H} \\ \text{CH}_3\text{.C . C . C . C . CHO} \\ \text{H H OH OH} \end{array}$$

hence the configuration of methyltetronic lactone (considered to be a γ-lactone) is $\begin{array}{c} \overline{\text{O}} \\ \text{OH H} \\ \text{CH}_3\text{.C . C . C . CO.} \\ \text{H H OH} \end{array}$ By passing dry ammonia gas into a solution of this lactone in ether we have prepared the crystalline amide of methyltetronic acid, the structure of which must be $\begin{array}{c} \text{OH OH H} \\ \text{CH}_3\text{.C . C . C . CONH}_2\text{.} \\ \text{H H OH} \end{array}$

Since the hydroxyl group is on the right of the asymmetric α-carbon atom

[1] *Ber.*, **35**, 2365 (1902).

[2] THIS JOURNAL, **39**, 1638 (1917).

[3] Fischer and Morrell, *Ber.*, **27**, 382 (1894); Fischer and Zach, *Ibid.*, **45**, 3761 (1912); Hudson, THIS JOURNAL, **31**, 345 (1910).

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of the amide it is to be expected[1] that the amide will be dextrorotary. This proves to be the case, its rotation in water being strongly to the right.

Experimental.

Methyltetronic Acid Lactone.—Fifty g. of crystalline rhamnose monohydrate was dissolved in 250 cc. of hot water and the solution was made up to 5250 cc. To this was added a solution of 93.5 g. of pure potassium hydroxide in 250 cc. of water. Air freed from carbon dioxide by passing over sodium hydroxide was then drawn through the mixture continuously for 3 days by the suction of a water pump. The diameter of the air inlet tube was 5 mm. The rate of flow was approximately 1.5 liters per minute. If the air is not admitted fast enough the solution will turn yellow, the color disappearing after several hours if the rate is increased. During daytime the solution was heated to 40–50°. At the end of the reaction the solution was colorless. Conc. hydrochloric acid was then added, the final addition being made with 10% acid using congo red paper as an indicator. The paper is pink in alkaline solution, takes on a light purple color when the organic sugar acids are liberated from their salts, and becomes dark blue fairly sharply when free hydrochloric acid is present. Acid was added just until the color became fairly blue, showing that the organic acids were entirely liberated from their salts but very little or no hydrochloric was present in the free state. The solution was then evaporated to dryness *in vacuo*. The distillate showed the presence of formic acid by reducing Fehling's solution. The white crystalline residue, somewhat gummy, was then boiled with absolute alcohol several times and filtered. The combined alcoholic solutions were then evaporated *in vacuo* to a thick red residue which was almost entirely soluble in ethyl acetate. This solution was filtered from the crystalline residue of potassium chloride. The ethyl acetate solution was evaporated on the steam bath, and the residue was triturated with warm ether until no more color dissolved. About 3 g. of a white crystalline substance was obtained from this ether extract by evaporating it almost to a sirup and letting stand several days. The residue that was insoluble in ether yielded about half a gram more of crystals of the same substance on standing in the open air several days.

The crystals melted at 121° and on recrystallization from absolute alcohol yielded 2 g. of needle-like crystals melting at 123°. A solution containing 0.3187 g. substance made up to 25 cc. with water rotated —1.14 circular degrees to the left in a 2 dcm. tube, hence $[\alpha]_D = -44.7°$. Methyltetronic acid lactone that was obtained by Ruff and Kohn from the oxidation of methyltetrose with bromine melted at 121° and had a specific rotation of —47.5°.

The crystals of this lactone are easily soluble in cold absolute ether, contrary to the behavior of most lactones of the sugar group. Ruff and Kohn describe the crystals as rather difficultly soluble in benzene, ether or

[1] Hudson, This Journal, 40, 813 (1918).

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chloroform and very soluble in alcohol or ethyl acetate. We have verified these statements except with reference to ether, which dissolves the crystals readily.

Methyltetronic Acid Amide.—One g. of methyltetronic acid lactone was dissolved in 30 cc. of cold ether and dry ammonia gas was passed through the solution for 20 minutes. An amorphous white precipitate settled out on the bottom of the flask. By rubbing it under ether with a glass rod for several minutes it became crystalline and could easily be filtered by suction. The yield was nearly quantitative. The substance was recrystallized from absolute alcohol, in which it was very soluble. The crystals were large plates which melted with decomposition at 135°.

A solution of 0.5404 g. substance made up to 25 cc. with water, using a 4 dcm. tube, showed a dextrorotation of 4.74 circular degrees; hence $[\alpha]_D = +54.8°$. Nitrogen was determined by the Kjeldahl method.

Calc. for $C_5H_{11}O_4N$: N, 9.40. Found: 9.30.

Optical Data on the Crystals of the Lactone and Amide.

Dr. Edgar T. Wherry has kindly supplied the following data:

Methyltetronic lactone under the microscope has the form of rods suggesting the rhombic system. The refractive indices, by immersion in oils, in which the substance is but slowly soluble, were $\alpha = 1.500$, $\beta = 1.515$, $\gamma = 1.535$, all ± 0.005. Double refraction strong, 0.035. In polarized light brilliant interference colors are shown, mostly of the third or fourth order. Extinction is straight. Elongation may be positive or negative. In convergent polarized light partial interference figures are frequently shown. The axial angle is large, $2E = 120° \pm 10°$. Sign positive.

Methyltetronic amide under the microscope shows irregular plates, of which the crystal system could not be determined. The refractive indices by immersion in oils, in which it appears to be insoluble, were $\alpha = 1.510$, $\beta = 1.530$, $\gamma = 1.560$, all ± 0.005. Double refraction very strong, 0.050. In polarized light brilliant interference colors of mostly second order were observed. No edges could be found on which to base extinction or elongation data. In convergent polarized light partial interference figures were often found, the axial angle being very large, and the sign probably +.

WASHINGTON, D. C.

NEW BOOK.

Essentials of Volumetric Analysis. By HENRY W. SCHIMPF, Ph.G., M.D., Professor of Analytical Chemistry in the Brooklyn College of Pharmacy. Third Edition. 366 + xiv pages. 61 figures. John Wiley and Sons, Inc., New York, 1917. Price, cloth, $1.60 net.

In the present, as in the earlier editions of this work, the United States Pharmacopeia has been taken as a basis, and the essential points have been reduced within the limits of a small book. The subject matter is arranged under 5 headings: Neutralization, Precipitation, Oxidation, Indirect Oxidation, and Iodimetry. The author has made some changes, discarding some obsolete processes and substituting new and up-to-date methods of analysis for them. Nomenclature has been revised in accord with the new

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Pharmacopeia. For example, the abbreviation "cc" for cubic centimeter has been replaced by the abbreviation "mil" for milliliter, and other changes have been made. The introduction of several new assay processes, among them being the assays of mercuric salts, phosphates, and hypophosphates by means of a standard sulphocyanate solution, the assays of chlorates, perborates, chloral, acetone, resorcinol, phenylsulfonates, arsenates, and alkali cacodylate, etc., have improved the book considerably. The 2 chapters on indicators and their uses are of value.

The book is marred by the author's disregard of the principles underlying the retention of significant figures, a notable example of which occurs on page 316, where the weight of 18.70 mils of oxygen is given as 0.02680832 g. Of the 7 figures given, only 3 or at most 4, are significant figures. Errors of this sort in text books are largely responsible for the careless usages in journal literature.

The author also ignores the best and accepted customs of writing equations in a manner to indicate molecular quantities of gaseous substances. Among numerous examples of this is the following from page 230: $K_2CrO_4 + 8HCl = 2KCl + 4H_2O + CrCl_3 + Cl_3$.

The illustrations, which were the subject of criticism in earlier editions, have not been improved.

The fact that this manual has passed to a third edition indicates that it more or less perfectly meets the needs of students of pharmacy, for whom it is mainly prepared. It is likely to prove somewhat less satisfactory to the general student or practitioner in analytical chemistry.

L. F. HAMILTON.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
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